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The National Measurement System for Surface Properties

C. J. Powell

Institute for Basic Standards
National Bureau of Standards
Washington, D. C. 20234

December 1976

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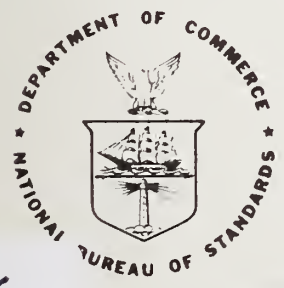

DEPARTMENT OF COMMERCE
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OPTICAL PHYSICS DIVISION SUMMARY REPORT

on a study of

THE NATIONAL MEASUREMENT SYSTEM FOR SURFACE PROPERTIES

C. J. Powell

Optical Physics Division
Institute for Basic Standards

EXECUTIVE SUMMARY

The large number of solid-surface properties that can be measured have been arbitrarily divided into two classes. First, there are the properties which can be used to characterize a surface: surface composition (as a function of position), surface atomic structure, surface electronic structure, the nature and distribution of surface defects, surface topography, and the nature and area of exposed facets. Second, there are derived properties of the surface characteristics as just defined and measures of the processes that occur on surfaces: electrical properties, optical properties, adhesion, bonding, catalytic activity, plating, durability, corrosion, decoration, grain-boundary segregation, lubrication, and reactivity. This report discusses directly only those measurements that are used for surface characterization with particular emphasis being given to the most common measurement, the measurement of surface composition, and lesser emphasis to the measurement of surface atomic structure and surface electronic structure. Measurement of surface topography is discussed in a separate report of this series by R. D. Young.

Throughout the report, the term "surface" is defined as the "outermost" layer of atoms of a solid. Thus, consideration is given primarily to those properties (and measurement methods) which are specific to the surface as defined. Some consideration is given also to the measurement of composition as a function of depth from a surface and at solid-solid interfaces.

A dramatic feature of this part of the National Measurement System is the rapid growth of surface science and surface technology and the substantial accomplishments that have been made in the past ten years. Surface science and surface technology are widely regarded as "frontier" areas in which major scientific breakthroughs will occur and major improvements in materials and processes will be developed.

Most of the measurement methods now in use for surface characterization have become commercially available within the past ten years. At this time there is a complete lack of standards, standard procedures, and standard materials to support surface-characterization measurements. In short, there is no established measurement system for the measurement of surface properties.

Most measurements of surface composition are now performed by Auger-electron spectroscopy and, to a lesser extent, by x-ray photoelectron spectroscopy, ion-scattering spectroscopy and secondary-ion mass spectroscopy. The sales of these instruments have been estimated to be about $10M per year with a current growth rate of 20 to 30% per year. About 60% of these instruments are in use in industrial laboratories, 20% in Federal Government laboratories, and 20% in university laboratories.

The surface-characterization measurements made in university and some other laboratories are frequently made to develop a fundamental understanding of the properties of relatively ideal (i.e., single-crystal) surfaces and of processes that occur on them. Surface-characterization measurements made in government laboratories support a variety of agency missions, ranging from national defense, space, energy, to the environment.

Measurements of surface composition are routinely made to solve an extremely wide range of industrial problems (of which examples are given). Most of these measurements are made in the semiconductor, chemical, petroleum, and metallurgical industries for applications ranging from process and device development, process control, process evaluation, to failure analysis. The economic benefits are difficult to estimate but are believed to be substantially greater than the corresponding costs.

Continued substantial growth in surface science and surface technology (and in the required surface-measurement capability) is

predicted for the the next five years. Present national goals for solution of the energy crisis, provision of an adequate defense capability, control of environmental pollution, increase of industrial productivity, and the development of advanced materials for improved individual health and safety and for the automobile and aircraft industries will require use of surface technology and improved surface-characterization measurements. Other factors which will stimulate growth in surface-measurement capability are projected developments in surface science, development of improved instrumentation, development of quantitative methods for surface characterization, legal needs, and anticipated growth in the applications of surface analysis.

Present surface-characterization measurements make use of reference data generated by instrument manufacturers, universities, government and industrial laboratories, and by NBS. Many important measurement needs have been identified, the most important, for surface technology, being to provide data and procedures to quantify measurements of surface composition. It is anticipated that the development of standards, standard procedures, reference data, and standard materials will be coordinated through the recently formed ASTM Committee E-42 on Surface Analysis.

Other measurement needs in surface science and surface technology have been identified. Many surface properties and processes depend on the surface composition, atomic structure, and particularly the surface electronic structure. It is anticipated that future developments in surface science will lead to a more detailed understanding of the mechanisms of catalysis, corrosion, adhesion, lubrication, and wear so that new materials with improved properties can be designed. Advances of this type depend on the development and application of new measurement methods to characterize disordered surfaces, highly dispersed catalysts, transient species on surfaces, the kinetics of reacting species, and the properties of such surfaces in their working environments.

NBS programs in surface physics have had considerable impact on surface science through the development of new instruments and measurement methods, the observation of new surface properties, the development of new theories and concepts, the provision of reference data, and the publication of data compilations and critical reviews. NBS data are also being used in surface technology. Additional NBS effort is required, however, to promote surface technology.

Seven recommendations are given for NBS action to improve and extend the measurement services required for the support of surface science and surface technology. Meaningful action by NBS and other interested groups should enable the establishment of a satisfactory National System for the Measurement of Surface Properties in the future.

1. INTRODUCTION

Surface properties are not only an integral part of our present culture ("beauty is only skin deep") but impact considerably on the properties of materials and the development of new technologies important for our industrial society. Processes and properties such as catalysis, adhesion, lubrication, durability, bonding, oxidation, passivation, plating, epitaxy, coating, doping, and crystal growth depend critically for their success or failure on surface characteristics. Likewise, the minimization of material or device failure (i.e., product reliability) can depend on the reduction of corrosion or wear, the absence of surface contaminants in the fabrication of semiconductor devices, or the nonoccurrence of embrittlement in metals caused by segregation of impurities to interfaces.

The history of surface science and surface technology in this century is interwoven with discoveries and developments in other branches of science and technology: the discovery of thermionic-, photo-, field-, and secondary-electron emission; the development of radio, x-ray, and special-purpose tubes; the discovery of electron diffraction; the developments of electron optics and electron-optical instrumentation; the investigations of the interactions of electrons, ions, neutral atoms and molecules, and photons with matter; the development of vacuum science and technology; the investigations of discharges in gases; the development of lamps; the development of semiconductor devices; the investigations of factors affecting the joining, working, wear, and polishing of metals; the investigations of corrosion and oxidation processes and the development of protective coatings; the studies of the adsorption, desorption, and reactions of gases on surfaces; and the development and characterization of improved catalysts. Many significant developments in surface science and surface technology, however, have occurred within the last ten years. We will show in this report that surface science has reached a stage of development such that knowledge of fundamental surface parameters can now be obtained. This growth has enabled the development of a new class of surface instrumentation that has been successfully applied to failure analysis, quality control, process evaluation and process development in the electronics, chemical, petroleum, and metallurgical industries. New national needs and the demand for improved materials and for new technologies have led to increasing demand for improved and more sensitive methods for characterizing surfaces and for measuring surface properties.

Throughout this report we will be discussing only the surfaces of solids; the properties of liquid surfaces, and solid/liquid interfaces, however, are of considerable importance in chemical technology and in biology. The term "surface" implies that there is a region in a given material where the properties are distinctly different from those of the "bulk." Likewise, the availability of scientific techniques and commercial instrumentation for the measurement of surface characteristics implies a particular depth sensitivity for the technique or instrument. For most of this report we will consider the ultimate definition of a surface, namely the outermost layer of atoms of the solid. We will use the term "surface region" to describe a region near the surface of less than ten atomic layers thickness. We therefore do not intend to discuss measurement techniques or properties that do not depend on or are not sensitive to the surface or surface region as just described. Measurements of surface finish and topography are discussed in a separate report of this series by R. D. Young.

A realization of the current importance and relevance of surface science and technology can be obtained from two comprehensive surveys concerning future directions in physics and opportunities in materials research conducted recently under the sponsorship of the National Academy of Sciences [1,2]. In "Physics in Perspective" an expert panel on physics of condensed matter has listed a number of topics of high current interest in that they are the concern of a large number of physicists and they represent areas in which major scientific breakthroughs appear likely. Surface physics was one such topic. We quote from this source [1]:

"Rapid advances are taking place in the characterization of the surfaces of solids, largely using new experimental techniques and the improved theoretical understanding of quantum mechanics as applied to interfaces. By characterization is meant a detailed specification of the chemical identity, geometrical position, and, ultimately, the electronic and vibronic structure of atoms at surfaces. The electronic, geometrical, and chemical behavior of defects and impurities adsorbed at the surface is another aspect of this problem. Also included in this category are the phenomena of tunneling in metal-insulator-metal, metal-insulator-semiconductor, and metal-insulator structures. Because of new experimental

techniques such as Auger spectroscopy, advanced electron microscopy, and ultra-high vacuums, rapid progress is being made. Entirely new methods for the control and preparation of interfaces have emerged from the vast amount of engineering and development carried out in recent years to produce integrated circuitry and other devices. The present rate of growth in this area offers the possibility of advanced understanding and control of chemisorption and catalysis."

In "Materials and Man's Needs," a distinguished panel has pointed out that improved materials are needed for major national goals, such as improved or new methods of energy generation, communication, transportation, health services, housing, management of the environment, and consumer goods [2]. The panel describes a number of frontiers in materials research that they believe will lead to improved materials and processes. Work on surfaces was one of the designated frontiers, and we quote the opinion of the panel to show the extensive impact of surface technology:

"Surfaces and interfaces are possibly one of the most fruitful research topics in materials science. Knowledge at the most fundamental level in this area can be expected to be relevant to almost all uses of materials, from the processing and performance of integrated circuits to the corrosion of structural components, from frictional wear and energy loss to catalysis and flammability, from crystal growth to adhesion. The variety and complexity of surfaces and surface layers are at least comparable to the variety and complexity of bulk properties, but our understanding of surfaces is, in contrast, in its infancy.

"The aim is to develop more sophisticated insight into the electronic and chemical properties of surfaces. These properties are very sensitive to the detailed ways in which atoms are positioned at the surface, however, and in general these positions are not known. Surface properties are related also to the properties of the underlying bulk material, but in ways that are not often clear. And though bulk properties, by-and-large, are understood in principle, if not always in detail, this is not true of many of the surface properties where the broad outlines of the phenomenology are only now being drawn. This phenomenology concerns, for example, the details and statistical mechanics of surface topology, local bond and electronic structures, the energy states of electrons at surfaces, and models for nucleation and growth.

"Surfaces offer an extra degree of freedom for the arrangement of atoms statistically on the lattice sites. The statistical mechanics of this situation, extending in three dimensions over several atomic layers, needs considerable development. The roughness of a surface on the atomic scale has a major impact on adsorption, surface diffusion, and crystal growth, but very little is yet known about the detailed role of surface roughness in these processes.

"The electronic properties of surfaces in simple systems warrant considerable attention. There is some controversy about the extent to which surfaces can be treated as an extension of the bulk--that is, whether the discontinuity in properties at the surface is great enough to require new concepts and analytical procedures. Our theoretical models for surface electronic properties, surface relaxation, and surface structure are rudimentary. The extent to which surface states on semiconductors are intrinsic to the surface or associated with surface impurities is under debate. Surface states occur both at free surfaces and at interfaces, such as the silicon-silicon oxide interface. It has been shown recently that various surface states on semiconductors correlate with various surface structures as revealed by low-energy electron diffraction.

"Surface nucleation, vapor deposition, adsorption, and surface contamination, topics with clear practical significance, are currently being investigated in detail for a variety of systems, with emphasis on the simpler systems. The kinetic and thermodynamic properties of vapor deposits can be obtained by mass spectrometric methods, and the distribution of clusters on the surface can be determined by diffraction methods. Classical surface nucleation theory is inadequate to account for the results of such measurements, and major modifications of the theory appear to be necessary. Adsorbed atoms can be identified by Auger spectroscopy, even at a small fraction of a monolayer coverage. Auger spectroscopy coupled with ion bombardment can be used for profiling, to get at bulk composition profiles below the surface. Low-energy electron diffraction is just entering the stage at which the position of surface atoms can be determined quantitatively with some accuracy. These methods are also being used extensively

to monitor the cleanliness and structure of surfaces and to investigate production problems involving contamination at surfaces. The electronic and chemical properties of surfaces and adsorbed species are being investigated by a variety of methods. X-ray photoelectron spectroscopy and ultraviolet photoemission spectroscopy are used to obtain band-structure data. Knowledge of electronic and chemical bonding can be derived from ion neutralization spectroscopy. Infrared reflection spectroscopy gives information about chemical bonding, and insights concerning deep electronic levels can be obtained from the analysis of Auger spectra.

"The techniques developed for surface research, such as ion mass analysis and Auger spectroscopy, are providing the best, and often the only, methods for investigating materials problems associated with thin films, grain boundary segregation, interdiffusion phenomena, and trace analysis. The trend toward miniaturization in electronics, resulting from economic, reliability, and high-frequency considerations, points toward growing importance of surfaces. The concepts of miniaturization are best embodied in the technology of large-scale integrated circuits, where surface and grain-boundary diffusion often dominate bulk diffusion processes. This trend is expected to continue, particularly as optical microcircuitry is developed.

"The elucidation of catalytic processes is not detailed in most cases. Considerable qualitative insight is available, but the roles of surface structure, surface defects, surface geometry, surface electronic properties, and even the bulk properties of catalysts have not been clarified in detail.

"Notable advances have been made in the area of adhesion, where knowledge of the role of adlayers and their interaction has contributed significantly. Friction is understood in some detail, especially the role and interaction of the asperities in sliding contact, but the processs is difficult to treat from a fundamental standpoint, let alone circumvent in practice. From a practical point of view, the lubrication of sliding contacts is fairly well understood, but cold welding can be a serious problem in electrical contacts. Erosion, corrosion, and contamination of electrical contacts as a result of arcing remain serious problems.

"Deeper knowledge of the behavior of surfaces can also be expected to improve our control over the important practical problem of corrosion--the interaction of a metal with its environment. The presence of water or an electrolyte solution changes the physics and chemistry of metal surfaces significantly. The surface energy is altered and becomes a strong function of the charge in the electrical double layer at the metal/solution interface. The equilibrium surface structure may be different from that in the presence of the metal's own vapor or in a vacuum, and it presents extra problems because the interface is not readily examined *in situ*. Some metals, such as silver, undergo surface rearrangement in aqueous solution at room temperature. Alloys generally undergo a change in their equilibrium or steady-state surface composition. The atomistics of these phenomena are poorly defined. There is much ignorance regarding the effects of surface stress, defect structure, and nonequilibrium conditions on the reactivity of metal surfaces, and these effects are of major importance in the performance of materials."

The latter report clearly shows the diverse and pervasive role of surfaces in current technology. Claims have been made over the last thirty years, however, that "surface science" or a particular, then new, technique would "solve" major problems or lead to dramatic improvements in major areas of surface technology such as catalysis and corrosion. Although some of these claims have been overoptimistic, the optimism of the above two National Academy of Sciences reports is warranted by the following significant developments in the last decade:

(a) The routine attainment of ultrahigh vacuum;

(b) The development of techniques to prepare and characterize surfaces;

(c) The extension of solid-state theory to surfaces;

(d) Mushrooming developments in surface science;

(e) The development of commercial instrumentation that can be used to measure surface structure and composition;

(f) The development of surface-related technologies (microelectronics, catalysis, controlled-thermonuclear-fusion reactors, corrosion) in response to material needs or problems (energy, pollution, defense, materials conservation, and productivity); and

(g) The successful use of surface instrumentation (e) to solve important surface-related problems (f).

Advances in surface science and technology depend on the availability and quality of measurements of relevant surface characteristics. We describe in this report the status of measurements now being made in surface science and surface technology and show the improvements in measurement capability that are needed. Most of the information for this report was collected and most of the writing was done in the spring of 1975. Some revisions and additions have been made in the summer of 1976 in response to recent developments.

2. STRUCTURE OF THE MEASUREMENT SYSTEM

2.1 Conceptual System

The conceptual base of modern surface measurements rests on conventions rather than on formal definitions adopted by statutory bodies. These conventions are rather general but have nevertheless been found useful by workers in the field. As will be pointed out in section 2.2, it appears likely that a more specific base will be established in the not too distant future for some surface measurements.

It is useful to consider the properties and characterizations of "ideal" and "real" surfaces. "Ideal" surfaces are those that are believed to have relatively simple structure and composition whereas "real" surfaces are those that are encountered in practice. Real surfaces can range from those prepared to approximate ideal surfaces as closely as possible (so that measured properties can be compared realistically with the results of calculations which are usually made for ideal surfaces) to those generated, for example, in a manufacturing process or those resulting from the failure of a component.

We can distinguish three types of ideal surfaces:

(a) A surface consisting entirely of a plane, single-crystal face of a material. It is implicitly assumed that the size of the exposed plane is large enough so "edge effects" do not affect the measurement being made; the minimum plane size may thus be a function of the measurement technique being used.

(b) A single-crystal surface as in (a) uniformly covered partially or wholly with known amounts of foreign atoms. The coverage of adatoms can vary typically from 1/1000 of a monolayer to several monolayers in the range of present interest.

(c) An interface consisting of two crystals with adjoining surfaces as defined in (a). The thickness of the crystals can be small (several monolayers, as in (b)) or large.

To adequately characterize a surface, it is often necessary to measure the following quantities [3]:

(1) The type of atomic species present on the surface;

(2) The arrangement or structure of the surface atoms;

(3) The electronic structure (principally of the valence electrons) of the surface atoms; and

(4) The motion of the atoms (atomic vibrations, surface diffusion, diffusion to and from the bulk, and evaporation).

These quantities are interrelated in the sense that a surface, like other physical systems, will relax after generation toward a configuration of minimum total energy. For example, a surface generated by a perfect cleave of a single crystal can relax by (i) modification of the atomic species on the surface (if the solid contains more than one atomic component), (ii) modification of the surface atomic structure with, in each case, (iii) resulting modifications of electronic structure and atomic dynamics.

We can also consider three types of real surfaces.

(A) Polycrystalline surfaces, with varying areas of single-crystal faces (facets) exposed and with varying amounts of defects (steps, pits, dislocations, scratches, etc.). The surfaces may vary in size from those of small particles (e.g., particulates or dispersed catalysts) to those of particular products or devices (e.g., integrated circuits, mirrors or weldments).

(B) Surfaces such as those described in (A) covered partially or wholly with foreign atoms to varying degrees of uniformity.

(C) Interfaces formed at the junction of two solid phases where the junction region can extend over a distance much larger than atomic dimensions.

Such surfaces generally need to be characterized by measurement of the quantities specified in items (1) through (4) above together with measurements of:

(5) The nature and distribution of defects on the surface;

(6) The surface topography;

(7) The nature and area of exposed facets;

(8) The spatial distribution of foreign atoms on the surface; and

(9) The depth distribution of different atomic species in the vicinity of interfaces.

"Complete" characterization of a surface on the scale indicated above is rarely attempted on account of the cost and complexity involved, the belief that certain types of characterization may not be required for a particular application, or the dynamic nature of surfaces. This last factor is extremely important; a surface can change its structure and composition as a function of time, either after generation, after heat treatment, after or during a particular surface-characterization measurement, or, more subtly, as the result of probe-sample interactions during what was intended to be solely a surface-characterization measurement.

We have outlined above the many ways in which a surface can be characterized. Measurements on surfaces, however, are made for a variety of purposes ranging from scientific to technological. For scientific applications, a surface will often have to be characterized fairly completely to test a theory or to gain a fundamental understanding of a particular property or process. For technological applications, the surface will generally have to be characterized to the extent necessary to relate to a particular phenomenon or the measurement of other surface-related properties. Such properties include:

(i) electrical properties (e.g., of integrated circuits);
(ii) optical properties (e.g., reflectance of mirrors);
(iii) adhesion
(iv) bonding
(v) catalytic activity
(vi) plating
(vii) durability
(viii) corrosion
(ix) decoration
(x) grain-boundary segregation
(xi) lubrication
(xii) surface reactions (e.g., fuel cells)
(xiii) biocompatibility

It is beyond the scope of this report to describe the nature and status of measurements of all surface-related properties, particularly as this is a relatively new and fast-growing area of activity. The discussion will instead be devoted predominantly to the surface characterizations that are commonly and can routinely be made with commercially available instrumentation, namely items (1), (2), (3), (8) and (9) above. (Measurement of surface topography is described in a separate report in this series.) Particular attention will be devoted to measurements currently required to advance surface science and to those required to advance surface technology. In the latter category, measurement of surface composition (items 1, 8 and 9 above) will be discussed at some length as it impacts directly on many other surface-related properties (items (i) through (xiii) above).

2.2 Basic Technical Infrastructure

2.2.1 Documentary Specification System

As noted in section 2.1 above, no formal standards or documentary specifications now exist for the characterization of surfaces, as defined earlier. This situation, however, is expected to change in the near future.

In March 1974, ASTM Subcommittee E-2.02 on Surface Analysis was formed. Four task groups have been formed (Auger-electron spectroscopy, x-ray photoelectron spectroscopy or ESCA, ion-microprobe analysis and secondary-ion mass spectroscopy, and ion-scattering spectroscopy) and it is anticipated that they will develop consensus standards for nomenclature, procedures, and reference materials for their respective techniques of surface analysis. In May 1976, this subcommittee was converted to a full committee (ASTM Committee E-42 on Surface Analysis) and the above-mentioned task groups were converted to subcommittees. ASTM Committee D-32 on Catalysts was formed in January 1975 to promote, *inter alia*, the development of test methods (such as surface chemical analysis) and materials pertaining to catalysts. In addition, a commission of the International Union of Pure and Applied Chemistry is drafting proposals for standardized nomenclature and data presentation for electron-spectroscopic methods of measurement in physical-chemistry experiments.

2.2.2 Instrumentation System

2.2.2.1 Measurement Tools and Techniques

A large variety of measurement techniques has been proposed for the characterization of surfaces. A summary of these techniques, adapted from a recent review of surface physics by Murday [4], is given in Appendix C while assessments of the scientific and technological utility of many of the techniques are given in a number of recent books and articles [3-53]. Many of these techniques are relatively new and/or undeveloped and, although they may give useful information concerning a surface, the

interpretation of the data may be complex or the technique may be restricted to special classes of materials. We will therefore restrict attention here to the more important techniques that are in widespread or growing use and, in the case of measurements in surface technology, to those for which appropriate instrumentation is commercially available. We should note, however, that the less-common techniques employed in surface-science experiments frequently make use of commercially available components. Also, new developments in surface science and improvements in instrumentation and techniques initially developed for applications in surface science usually precede further development by instrument manufacturers and others for ultimate application in surface technology.

We will discuss in this report the following types of surface-measurements.

(1) Measurement of Surface Composition
  (a) Auger-electron spectroscopy (AES)
  (b) X-ray photoelectron spectroscopy (XPS)
  (c) Ion-scattering spectroscopy (ISS)
  (d) Secondary-ion mass spectroscopy (SIMS), including ion-microprobe mass analysis (IMMA) and secondary-ion imaging mass spectroscopy (SIIMS)
  (e) Appearance-potential spectroscopy (APS)
  (f) Field-ion microscope - Atom-probe spectroscopy (FIM-APS)
  (g) Field-desorption spectroscopy (FDS)
  (h) Internal-reflectance spectroscopy (IRS)
  (i) Inelastic electron tunneling spectroscopy (IETS)
  (j) Rutherford backscattering spectroscopy (RBS)

We will discuss the means by which spatial variation of composition across a surface can be obtained and how the depth-variation of composition can be measured.

(2) Measurement of Surface Atomic Structure
  (a) Low-energy electron diffraction (LEED)
  (b) Field-ion microscopy (FIM)
  (c) Field-desorption spectroscopy (FDS)
  (d) uv photoelectron spectroscopy (UPS)
  (e) Electron-stimulated desorption of ions (ESDI)
  (f) Auger-electron spectroscopy (AES)
  (g) Ion-scattering spectroscopy (ISS)
  (h) Electron energy-loss spectroscopy (EELS)
  (i) Internal-reflectance spectroscopy (IRS)

(3) Measurement of Electronic Structure at Surfaces
  (a) X-ray photoelectron spectroscopy (XPS)
  (b) uv photoelectron spectroscopy (UPS)
  (c) Auger-electron spectroscopy (AES)
  (d) Electron energy-loss spectroscopy (EELS)
  (e) Field-electron energy spectroscopy (FEES)
  (f) Ion-neutralization spectroscopy (INS)
  (g) Appearance-potential spectroscopy (APS)

There are additional measurement techniques (e.g., ellipsometry) that are extremely useful for monitoring changes of surface composition or of film thickness but which will not be discussed here as they cannot be used to identify the specific elements present on a sample.

A schematic outline of the techniques listed above is shown in table 2.1. Here,

Table 2.1 Outline of surface measurement techniques discussed in this report. An asterisk denotes a technique for which instrumentation is manufactured in the U.S. while a dagger denotes a technique for which instrumentation is marketed in the U.S. from foreign sources.

Incident Probe \ Detected Particle	Photons	Electrons	Ions
Photons	IRS*	XPS*† UPS† AES-XE*†	
Electrons	APS	AES-EE*† EELS*† IETS LEED*†	ESDI
Ions		INS	ISS* RBS* SIIMS† SIMS*† IMMA*†
Electric Field		FEES	FIM

as with the other surface-measurement techniques, we have an "incident probe" on a sample surface. The incident probe can be an atom (or molecule), an ion, an electron, a photon, or an electric or magnetic field. The experimenter observes a scattered or secondary particle (atom, ion, electron, or photon) that results from the interaction of the probe with the sample. The variety of techniques involving incident or detected electrons listed in table 2.1 is an indication of their importance in surface measurements. The surface sensitivity of many of these techniques is in fact due to the very large interaction cross sections for low-energy electrons in solids. We finally note that Auger-electron measurements can be performed either with electron excitation (AES-EE) or with x-ray excitation (AES-XE).

Particular attention will be devoted in this report to item 1 above since measurements for the determination of surface compositions are of considerable importance now in surface science and technology. Measurements of surface atomic structure and of surface electronic structure are of considerable importance in surface science on account of their anticipated impact in surface technology (e.g., by understanding and controlling mechanisms of catalysis, bonding, and corrosion and through development of improved semiconductor thin-film or electrochemical devices).

It should be emphasized that most of the techniques listed in table 2.1 are relatively new or currently undergoing rapid development in scope, techniques, or accuracy of measurement. (Use of the word "new" in this context implies a time of less than ten years since the technique was proposed or demonstrated scientifically.) To illustrate this point, figure 2.1 shows the number of papers published per year in x-ray photoelectron spectroscopy (XPS), Auger-electron spectroscopy (AES), and combined AES and low-energy electron diffraction (LEED) for years where this information is available in bibliographic form [54-56]. Although LEED was discovered by Davisson and Germer in 1927, it has not been used or applied extensively except during the past ten years. In fact, it has only become possible in the last several years for the surface structures and lattice constants of clean single-crystal surfaces to be obtained routinely from LEED data with reasonable accuracy, and it is only in the last two years that surface structures, bond sites and bond lengths have been similarly deduced for adsorbates on single-crystal surfaces. Likewise, figure 2.1 shows the tremendous growth in XPS and AES that has occurred in the last five to seven years. Inspection of the subject indexes of journals which publish articles on surface science and technology shows that there has been substantial growth in the use of all surface-characterization methods over the last four years; a recent bibliography on AES shows that there were about 500 papers on this subject published in 1975 [55(b)].

At this time, there are no formal standards or procedures for the operation and calibration of surface instrumentation (specifically for the techniques shown in table 2.1) or for the analysis of measurement data. Each experimenter is expected to do the best he can based on his own training and experience and using the sometimes conflicting data, spectra, and analytical procedures.

2.2.2.2 The Instrumentation Industry

Complete instruments or components for the measurement techniques listed in table 2.1 can be purchased from the manufacturers shown in table 2.2. We show here present and former manufacturers of this equipment listed alphabetically according to whether the equipment is made in the U.S. or whether it is made elsewhere and marketed in the U.S. The information for this table was obtained from recent exhibits of surface-measurement equipment (Joint Meeting of the Electron Microscopy Society of America and the Microbeam Analysis Society, Las Vegas, August 1975; American Vacuum Society, Philadelphia, October 1975; and the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1976), listings in recent directories of scientific instrumentation [57-59] and a recent survey article [17].

Based on an awareness of published literature, contacts with many of the manufacturers listed in table 2.2, a recent analysis [60] of the analytical-instruments market, and a survey of instruments on exhibition at the 1976 Pittsburgh Conference [61], we have identified AES, IMMA, ISS, LEED, SIMS, and XPS as the surface-measurements techniques with the greatest number of U.S. users. Most domestic manufacturers of these types of equipment were requested in early 1975 to provide information concerning their instrument sales and their purchasers. Information on sales was solicited in an attempt to determine the size of the instrument market, the extent to which these instruments are deployed, and the economic significance of these surface measurements in this part of the National Measurement System. Information concerning identity of

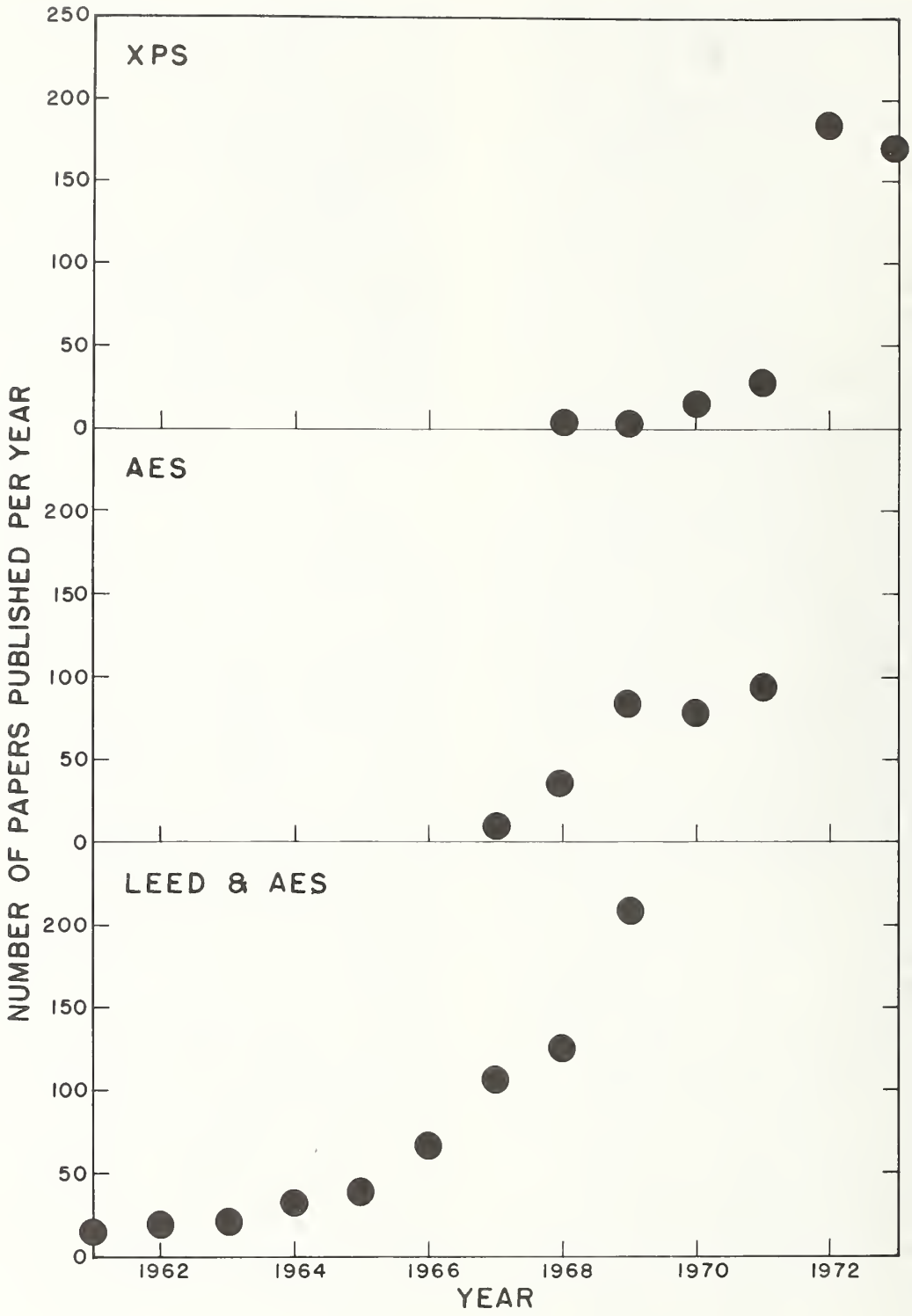

Figure 2.1 Number of papers published per year in x-ray photoelectron spectroscopy (XPS), Auger-electron spectroscopy (AES), and combined AES and low-energy electron diffraction (LEED) from recent bibliographies.

Table 2.2. Present (X) and former (F) manufacturers of surface-measurement equipment based on the techniques listed in table 2.1.

Manufacturer	Measurement Technique									
	AES-EE	AES-XE	EELS	IRS	ISS	LEED	RBS	SIMS	UPS	XPS
(a) U.S. Manufacturers										
Advanced Metals Research	X									
Applied Research Laboratories								X		
Coates and Welter	X									
Commonwealth Scientific								X		
Dupont		X								X
Etec	X							X		
Extranuclear Laboratories								X		
GCA/McPherson		X							X	X
General Ionex							X			
Harrick Scientific				X						
Hewlett-Packard		F								F
Nuclide								X		
Physical Electronics	X	X	X			X		X	X	X
3M					X			X		
Varian	X	F	X			X				F
Wilks Scientific				X						
(b) Foreign Manufacturers										
AEI (U.K.)		X						X		X
Balzers (Lichtenstein)								X		
Cameca (France)								X		
Hitachi (Japan)								X		
JEOL (Japan)	X	X	X					X		
Leybold-Heraeus (Germany)	X	X	X					X	X	X
Riber (France)	X		X							
VG Scientific (U.K.)	X	X	X			X		X	X	X

customers or classes of customers was sought to determine the extent to which these instruments are being used in surface science and technology (in either government, academic, or various types of industrial laboratories) and, through personal contact of selected customers, the nature of the use to which the instrument has been put. A report on the results of the latter inquiries is given in section 3.

Sales information is understandably regarded as proprietary information but most manufacturers approached were cooperative in providing confidential customer lists or informal estimates of their instrument sales and either the identity of representative purchasers or information concerning the distribution of customers in different groups. The former information is summarized in table 2.3.

A number of comments should be made about the information contained in table 2.3. First, the estimate of total numbers of instruments is based on sales and estimates provided almost entirely by the U.S. manufacturers; no similar inquiries were made of foreign companies. The numbers of instruments shown thus reflects sales of U.S. instruments within the U.S. and abroad and a very coarse estimate of sales by foreign companies in countries other than the U.S. Second, the total number of instruments for each measurement technique cannot be simply intercompared without consideration of the time when the technique became "popular" (cf., fig. 2.1) and of the related time when commercial instrumentation became available from different companies. Third, the estimate of average cost per installation is of necessity rather crude. The cost of XPS instrumentation, for example, can vary widely depending on the manufacturer and the number of "options" selected by the purchaser. In addition, LEED optics or a high-performance AES analyzer can be purchased as components (with or without the related commercial control and recording electronics) to be installed on an existing vacuum system. Fourth, it is difficult to verify the information concerning gross sales that was supplied by a few manufacturers. Nevertheless, the approximate total capital investment in AES, ISS, LEED, SIMS, and XPS equipment of about $50M shown in table 2.3 is consistent with the independent findings of Frost and Sullivan, Inc. in a recent analysis [60].

Approximately half to three-quarters of the instrumentation summarized in table 2.3 has been sold to purchasers in the U.S. Of this fraction, it is estimated that about 60% of the instrumentation is in industrial laboratories, about 20% in Federal government laboratories, and about 20% in university laboratories. The total U.S. capital investment in this instrumentation is believed to be greater than $40M. Contacts with manufacturers and surveys of users and potential users by *Research/Development* magazine (the respondents were predominantly chemists and analytical chemists) indicate that the growth rate in instrument sales is about 20 to 30% per year and that the annual sales volume of LEED, XPS, AES, and ISS/SIMS equipment is about $10M per year [62].

2.2.3 Reference Data

As pointed out earlier (cf., Appendix C), many techniques are employed for the characterization of surfaces and reliable reference data is of vital importance in both surface science and surface technology. Reference data is understood to mean:

(a) data on observed positions and intensities of spectral features measured for some material by a particular technique;

Table 2.3. Estimated number, individual average cost, and total capital investment in commercial LEED, AES, XPS, and ISS/SIMS instrumentation (worldwide).

Measurement Technique	Estimated Total Number of Instruments	Approximate Average Cost of Instrumentation	Approximate Total Capital Investment
LEED	150-200	$50K	$8.75M
AES	500-600	$50K	$27.5M
XPS	120-150	$100K	$13.5M
ISS/SIMS	40	$65K	$2.6M
IMMA	60	$300K	$18M
		Total	$70M

(b) theoretical, experimental, and analytical data on the "measurement process" for a particular technique; and

(c) data concerning the fundamentals of the interactions of the "incident probes" and "detected particles" (cf., table 2.1) with samples and surfaces of varying degrees of crystalline perfection, homogeneity, stability, and reactivity.

Reference data is frequently generated by workers in surface science and disseminated in the form of publications in appropriate professional journals. Summaries of such data appear from time to time as reviews or as books (for example, refs. [3] to [53].

Due to the embryonic nature of surface science and technology, there is at present a serious lack of adequate reference data, particularly for the more widely used surface-measurement techniques shown in table 2.1. Users of AES equipment, for example, in the chemical, petroleum, metallurgical, and semiconductor industries as well as in government and university laboratories need reliable reference data to enable them to identify surface contaminants or to determine the composition of a surface following a particular process. In addition, they need to have a methodology to convert observed intensities to sample composition and to have appropriate sputtering data if composition-versus-depth information is required. Users of this type need reference data in order that they can solve surface problems important to the company or industry as readily as possible. Without this information, the work is impeded or decisions are made from inadequate or unreliable data.

2.2.4 Reference Materials

No reference materials are produced at this time for applications in surface science and technology. The need for such materials has been strongly expressed, however, by ASTM Committees E-42 and D-32 and by many individuals contacted in connection with this study.

Two types of reference materials are needed for applications that require surface analyses. First, there is the need for pure materials to calibrate the energy and intensity scales of electron spectrometers (for AES and XPS) and the intensity scale of mass spectrometers (for ISS, IMMA, and SIMS). Second, standard materials are needed for the determination of relative surface composition (to obtain the stoichiometry) or the absolute surface composition (to obtain surface density of atoms) in many different types of systems (alloys, impurities on or near a surface, or a thin film on a substrate) for a wide variety of applications in the metallurgical, semiconductor, chemical, and catalyst industries. Such reference materials would be used to establish calibration curves to obtain compositions from observed intensities, to establish sensitivity limits for the presence or absence of key atoms or contaminants on surfaces, or to obtain performance data on "depth profiling" (the determination of composition versus depth from a surface by the process of sputtering).

Careful measurements are required for both types of reference materials to establish their properties (e.g., electron energies and relative intensities) with the desired accuracy. Also, it is necessary to ensure that the surface of a reference material can be cleaned or regenerated in a particular instrument.

It is expected that reference materials will also be used in "round robins" to intercompare measurements made in different laboratories by the same measurement technique or by different measurement techniques. These intercomparisons and the related reference data will eventually form the basis for a satisfactory measurements assurance program for the analysis of surfaces.

2.2.5 Science and People

Surface science and technology are interdisciplinary activities presently involving physicists, chemists, and metallurgists. This diversity of involvement can be appreciated by the many professional societies or organizations that support publications or sponsor meetings in which surface properties figure prominently. These societies or organizations include (in the U.S.):

(1) American Physical Society
(2) American Vacuum Society
(3) American Chemical Society
(4) Physical Electronics Conference
(5) Electrochemical Society
(6) Microbeam Analysis Society
(7) The Metallurgical Society
(8) Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy
(9) Federation of Analytical Chemistry and Spectroscopy Societies
(10) American Society for Testing and Materials
(11) Gordon Conferences
(12) Electron Microscopy Society of America
(13) Scanning Electron Microscope Symposium.

Analogous professional societies and organizations are active in other countries.

The scientists working on the frontiers of surface science typically have the Ph.D. degree. Although of necessity they have received training in a particular area of a particular discipline (e.g., physics), many have had to become proficient in the language and the body of knowledge of related areas of other disciplines (e.g., chemistry). There are also many scientists who are concerned primarily with measurement of bulk properties of solids (perhaps using the surface as a "window" for the solid) who have of necessity become familiar with surface processes and problems both to prepare samples of the needed purity and to obtain valid data.

There is a growing number of scientists and technologists in analytical and other industrial laboratories who are now routinely using instrumentation (AES, XPS, SIMS/IMMA, and ISS) to determine surface composition and properties. These people have a diversity of backgrounds with relatively few having had appreciable previous experience in surface science or closely related fields. For example, some of these people would be familiar with operation of the electron-probe microanalyzer; this instrument, however, operates at high vacuum rather than at ultrahigh vacuum (as in surface-analysis instrumentation) and the sampling depth is typically 10 000 Å rather than 10 Å. Thus, because of insufficient familiarity with the new surface-analytical instrumentation and perhaps because of inadequate training, a buyer may find himself ill-equipped to make sound purchasing decisions and a user may be unable to cope with day-to-day subtleties in specimen preparation and in operation of the equipment. There is thus a strong and growing need for short courses and workshops that will provide up-to-date surveys of the capabilities of different surface-measurement techniques and that will help users of particular equipment to operate their instrumentation more effectively. Short courses of this type have been sponsored over the last several years by some professional societies, several universities, and some instrument manufacturers and have been well attended.

Most of the new developments in surface science and surface technology appear in archival journals published by professional societies and by commercial houses. Information from journals is reviewed, distilled, and highlighted in a variety of books and publications ranging from "Reviews of Modern Physics," "Annual Review of Physical Chemistry," "Analytical Chemistry" (and many others [3-53]) to "Research/Development" and "Industrial Research." The large number of surface-measurement techniques (Appendix C and table 2.1) and the rapid pace of scientific and instrumental developments are such, however, that there is a continuing need for up-to-date evaluations of instruments, techniques, and methods of data analysis for specific types of applications. Review articles, short courses, and workshops are again required to meet this need.

2.3 Realized Measurement Capabilities

As pointed out in section 2.2.2.1 and in Appendix C, there are many techniques by which surfaces are characterized. In addition, there are many properties of solids (e.g., electrical, optical, reactivity, bonding, durability) that depend on the nature and state of the solid surface, as noted in section 2.1. A comprehensive review and analysis of methods to characterize surfaces and to determine surface properties for the many types of materials and applications would be voluminous. Since the status of surface-characterization methods has been described in recent review articles and books [3-53] and related techniques have been described elsewhere [63,64], we will give a brief assessment of only those forms of surface characterization that have been judged to be most significant, namely, items (1), (2), and (3) listed in section 2.2.2.1. These will now be discussed in turn.

2.3.1 Measurement of Surface Composition

Several techniques are now used for qualitative analyses of surfaces. Quantitative analyses of surfaces are not now possible on a routine basis although data for an unknown sample can be compared usefully with data from a local standard prepared by the user if the composition of the standard approaches that of the unknown; this method is not feasible or efficient for many users. Practically all respondents contacted during this study emphasized the pressing need for quantitative surface analyses.

The phrase "quantitative surface analysis" needs to be defined because "analyses" can be performed in a number of ways depending on the problem to be solved and on the sample. Ideally, one might want to know the composition as a function of position of a multicomponent sample. More simply, one might want to be able to say that a certain amount of a particular element or compound is present in the surface region of a sample. For example, one might want to know the coverage of an adsorbed or condensed atomic or molecular layer on a surface or to say that the contamination on a surface is less

than some desired amount. In other cases, one might want to measure the composition of a bicomponent system which could possibly be homogeneous or inhomogeneous. Finally, it is frequently desired to determine the concentration of particular elements as a function of depth from the surface and as a function of position on or near the surface. Although one may be able to define the type of analysis that is desired in a particular application, the success in obtaining the desired analysis depends on the homogeneity of the sample, the extent to which particular phases are localized on the surface or in the bulk, and the sensitivity, specificity, spatial resolution, and applicability of a particular analytical method.

The concentration of a particular element as a function of depth from the surface is now generally obtained through continuous or successive sputtering of the surface, whatever measurement technique is used to determine the surface composition at a particular time [7]. Measurements of this type are of considerable importance in analyzing, for example, the diffusion of dopants and impurities in thin film and semiconductor devices, the variation of composition in the vicinity of grain boundaries, and the differences between surface and bulk compositions of alloy catalysts. Unfortunately, very little reliable information is now available concerning sputtering rates, their dependence on ion species and energy, their variation with crystalline perfection and orientation, and their variation with compounding or alloying. In addition, data need to be obtained on the extent to which ion bombardment causes dissociation of compounds, stimulates diffusion, causes lattice damage, or generates ridges, steps, cones, facets, and protrusions on the surface [7]. To obtain reliable concentration-depth information, one also needs to know the current density and current density distribution of the ion beam at the sample and must avoid errors associated with edges or shadows of the crater formed by sputtering; the effects of small variations of current density in the ion beam can be minimized, however, by scanning the ion beam across the surface. The depth resolution obtained during sputtering depends on the uniformity of ion current density, damage to the sample during sputtering, redeposition of sputtered material, the sensitivity of the particular measurement technique for the particular sample, and the intrinsic sampling depth of the measurement technique for the particular material. These and other complicating factors have been discussed in several recent articles [65-67].

We will now briefly describe the several techniques listed in section 2.2.2.1 for the determination of surface composition and give a semiquantitative estimate of the measurement capability that has now been attained for routine conditions of operation. The numerical measures given here should not be construed necessarily as "best" or "limiting" levels of performance nor should they be used with the limited information given here to "rate" one technique against another. As Park [5] has clearly pointed out, sensitivity is a function of spatial resolution and the related flux of "probe" particles, resolution of the detection system, bandwidth, background level in the vicinity of the "signal," the noise-power spectrum, and changes in the sample caused by the incident probe or by exposure to the residual atmosphere of the vacuum system. That is, the degree of success or applicability of a particular measurement technique depends greatly on the details of the measurement process (i.e., the relevant physics and chemistry) and on the nature of the measurement or analytical problem. A more extensive discussion of the analytical performance of these measurement techniques is given in a recent review by Coburn and Kay [7].

The most common method for determination of surface composition is Auger-electron spectroscopy (table 2.3). All elements with atomic number greater than 2 can be detected and in most work to date only elemental identifications have been made. The latter situation is attributed to the fact that early AES measurements were frequently performed with LEED instrumentation which had relatively poor energy resolution. The resolution of commercial AES electron energy analyzers has improved in recent years to the point where changes in peak positions and in peak shapes can be observed and correlated with the chemical environment of the particular element. Identification of chemical compounds by this technique is at an early stage, but it is anticipated that considerable progress in this direction will be made in the near future. The sensitivity of AES in typical measurement situations can be of the order of 0.1% of an atomic layer [68,69]. The sampling depth of AES is usually between 3 and 20 Å, depending on the sample, while the lateral resolution obtained in recently introduced scanning Auger-electron microscopes can be as low as about 0.1 μm. The incident electron beam can cause damage (dissociation, desorption, polymerization, lattice changes) in some samples but these effects have yet to be adequately quantified.

X-ray-photoelectron spectroscopy (XPS), also known as ESCA, can be used to detect all elements although identification of hydrogen is difficult in most cases. The pioneering work with this technique was performed at Uppsala University with modified high-resolution β-ray spectrometers. An important early result was that relatively small "chemical shifts" of photolines occurred for an element in different chemical compounds. Such observations have led to the introduction of x-ray monochromators of improved performance and to deconvolution methods to obtain improved resolution. The sensitivity of XPS measurements is comparable to that of AES [28,70-72] although surface enrichment techniques have been used to greatly extend the surface specificity to the ppb level [73,74]. The sampling depth in XPS is comparable to that in AES. Although damage by the incident x-ray beam has been observed, it seems to be much less than that found when incident electrons are used to obtain comparable information. Auger-electron peaks are also observed in XPS spectra and can give useful additional information (e.g., by identifying elements for which the XPS peaks overlap or through larger observed chemical shifts [75]).

"Matrix effects" can modify intensities through variations of electron transport in different samples, through variations of electron backscattering in AES, and through "shake-up" or "shake-off" effects in both AES and XPS [7]. The surface sensitivity in both AES and XPS can be enhanced, if desired, by collecting electrons emitted at near-grazing angles to the surface.

Ion-scattering spectroscopy (ISS) with ion energies less than 10 keV can be used to detect all elements except hydrogen and helium with a sampling depth of one monolayer, independent of material. The sensitivity is also about 0.1% of an atomic layer, but the scattered-ion yield depends on matrix and neutralization effects and on oscillations in the scattering cross sections with ion energy [25,76-78]; these effects are only partly understood [26,76-79]. Lateral variation of surface composition can be obtained by scanning the ion beam across the sample, at present with a resolution of about 100 μm. Information concerning the sample composition below the surface can be obtained with incident ion energies much greater than 10 keV (e.g., helium ions with energies up to 2 MeV), a technique then known as Rutherford backscattering spectroscopy (RBS) [80]. Complications in analyses can arise on account of channeling in crystalline materials as well as sensitivity and mass-resolution limitations caused by multiple scattering and ion energy loss [77,80].

The secondary ions emitted from surfaces under ion bombardment can be mass-analyzed to give surface-composition data; this technique is referred to as secondary-ion mass spectroscopy (SIMS) or, with a narrow (∿ 1 μm) incident ion beam, as ion microprobe mass analysis (IMMA). Alternatively, the sample can be bombarded with a relatively broad ion beam (∿ 100 μm) and an image of the sample obtained with secondary ions [i.e., a secondary-ion imaging mass spectrometer (SIIMS)] with a lateral resolution of about 1 μm. All elements can be detected but there are large (many orders of magnitude) variations in detection efficiency from element to element and large matrix effects [81-84]. The sampling depth and thus the depth of surface sputtered is a function of the sensitivity and the beam area; it can vary from about 2 to 100 Å [81-84].

Appearance-potential spectroscopy (APS) is a relatively simple technique. Unfortunately, it can be used to detect only a limited number of elements for reasons that are not now clear [85]. The sampling depth is usually between 3 and 20 Å, depending on the material, but the sensitivity has recently been improved to the point where chemisorbed species on a surface can be detected [86].

Identification of surface atoms can be accomplished by field-ion microscopy atom-probe spectroscopy (FIM-APS) [87] and by field-desorption spectroscopy (FDS) [88]. Both techniques represent developments of the field-ion microscope and can be used with a limited number of solids. In each case, the identity of the topmost layer of atoms on a specimen surface is obtained; by successive field desorption, composition versus depth information can be obtained.

Two measurement techniques that appear to be of growing utility for the determination of surface composition are internal reflection spectroscopy (IRS) [89-92] and inelastic electron tunneling spectroscopy (IETS) [93-96]. The IRS technique can be used to detect about 4% of a monolayer of chemisorbed gas (in the favorable case of CO) on a metal surface [88]. The IETS technique can be used to detect vibrational excitations of molecules condensed at a metal-insulator interface in a metal-insulator-metal junction. Although the nature of the IETS technique precludes its application to arbitrary surfaces, it can be useful in detecting small quantities (e.g., a few percent of a monolayer) of organic molecules deposited on an insulating surface [90-92].

2.3.2 Measurement of Surface Atomic Structure

While the bulk crystalline structure of many solids has been determined by x-ray diffraction and electron diffraction measurements, relatively little is known about the equilibrium arrangement of atoms at surfaces and the changes that occur with various surface treatments.

The technique now in most common use for the determination of surface atomic structure is low-energy electron diffraction (LEED) [50]. Analysis of the data is complex and only recently have acceptable solutions for the structures of a number of clean metal single-crystal surfaces been determined [9,11(b),11(f),97]. The structures of ordered adsorbates on single-crystal surfaces have also recently been derived, and it is anticipated that there will be a great deal of progress in determinations of surface structures in the next few years [97,98]. A promising possibility is the use of polarized electrons in diffraction experiments to obtain surface structures [99].

The diffraction patterns observed in conventional LEED instruments are due to ordered regions of sizes up to about 100 Å (the typical coherence width of the electron beam). Steps and other surface imperfections will modify the electron intensity distributions [100-103], as well as other surface properties [102-104].

The field-ion microscope (FIM) can be used to obtain detailed information concerning the arrangement of surface atoms for a limited number of solids that can be shaped with a tip of radius $\lesssim$ 1000 Å and which can withstand an electric field near the surface of 10 to 50 GV/m [35,87]. The magnitude of the applied field can be reduced with use of an image intensifier. Information about the surface structure of particular atomic species can be obtained with atom-probe spectroscopy (FIM-APS) [87] or with field-desorption spectroscopy (FDS) [88].

In the last two years, several measurement techniques have been proposed for determining the *local* atomic structure of clean and adsorbate-covered surfaces. Although detailed theories of the processes have to be developed and the range and accuracy of the techniques have to be demonstrated experimentally, these developments hold the promise that information concerning the sites and bond geometries of surface atoms can be obtained in a fairly direct manner. The LEED technique, on the other hand, is based on coherent electron scattering from ordered atomic arrays (i.e., long-range order), and bond geometry information has to be obtained from a relatively complex analysis of a large amount of data.

It has been shown theoretically that atomic-structure information can be obtained from the angular distribution of photoemitted electrons [105-107]. Several experiments have been performed that show significant anisotropies in the photoelectron angular distributions for chemisorbed atoms on surfaces [108,109] and from clean surfaces [110,111]. These and other similar experiments indicate that data on bonding sites and directions of surface atoms can be derived from UPS measurements. Angular anisotropies have also been observed in the emission of Auger electrons in AES experiments but it appears that these anisotropies are not as sensitive to local structure as UPS experiments [112].

Anisotropies have been found in the angular distribution of ions desorbed from adsorbate-covered surfaces under electron bombardment [113]. These anisotropies in ESDI experiments are related to the local bonding of the adsorbate on the surface [114] and have been compared and contrasted with corresponding LEED measurements [113].

Atomic-structure information can be obtained from ISS experiments [25,26,115]. Use here can be made of the fact that a surface atom (e.g., an adsorbate) has a shadowing effect with respect to nearby atoms. Alternatively, multiple scattering can be important (usually for higher ion masses, smaller ion energies, and smaller angles of incidence and scattering) and give information about bond distances and geometries.

The vibrations of surface atoms can be directly measured by IRS [89-92], IETS [93-96], and EELS [116,117]. The measured energies for the vibrational excitations are related, in part, to the bond geometries and it appears that the geometries of adsorbates in different surface binding sites can be determined.

The technique known as extended x-ray absorption fine structure (EXAFS) has been shown to be useful for determining the local atomic arrangement and atom-atom spacings in solids and molecules. It now seems likely that surface sensitivity can be obtained by measuring the yield of Auger electrons (emitted following x-ray absorption) as the x-ray energy is varied [118]. Thus, the geometries of surface atoms (particularly of adsorbates on surfaces) could be determined by this method.

2.3.3 Measurement of Electronic Structure at Surfaces

Many techniques have been used to measure the electronic structure at surfaces [3,5, 8,10-15,18,31,33,35-50], that is, the spatial charge distribution and the energy distribution of the electronic states of the surface atoms. The most common and useful techniques are: x-ray photoelectron spectroscopy (XPS) of valence electrons [11(c),12,18,24,40,47, 119]; uv photoelectron spectroscopy (UPS) [11(c),12,39,47,119]; Auger-electron spectroscopy (AES) involving valence electrons [40,47,50,120]; electron energy-loss spectroscopy (EELS) [5,22,121]; field-electron energy spectroscopy (FEES) [11(e),122]; ion-neutralization spectroscopy (INS) [13,123]; and appearance-potential spectroscopy (APS) [5,85,86]. A review of methods for calculating the electronic structure of surfaces has been published recently [124].

All of these techniques involve electrons as the incident or detected particles or both. With the exception of FEES and INS, the surface sensitivity of the techniques is due to the short inelastic mean free path ($\sim$ 3 to 20 Å) of low-energy electrons ($\sim$ 10 to $\sim$ 1000 eV) in solids. With the exception of FEES, all techniques involve an electronic transition or excitation. The observed spectral information is thus related to the valence electron density of states and to a transition probability appropriate for the particular process. Additional complexities can arise, and these can be regarded as making the determination of the density of states more difficult or as giving additional useful information about the surface. The complexity of the measurement process, however, often makes it desirable to compare, contrast, or combine results obtained by more than one measurement technique. One technique, FEES, is relatively well understood [11(e)], but unfortunately it is of less general applicability than the others.

Despite the complexity in the interpretation of many of the measurements, a large amount of significant information on surface electronic structure has been obtained during the past five years. Surfaces of metals, insulators, alloys, and semiconductors have been examined. Surface states have been observed on semiconductor surfaces, as expected, and also on some metal surfaces. Different electronic structures have been found on different crystal faces of a material and related to the bulk band structure. The presence of single atoms on otherwise clean surfaces has been detected and their electronic structure characterized. Different binding states of adsorbed atoms and molecules have been observed with different electronic structure. The initial stages of oxidation and corrosion have been detected and an understanding gained of some of the basic processes. Intermediate species in a prototype catalytic reaction have been observed and monitored as a function of surface temperature. Surface-electronic properties are being related to the symmetry and directionality of surface bonds.

The various measurement techniques for determining electronic structure at surfaces have been reviewed recently and extensively elsewhere [5,8,10-15,18,31,33,35-50,120-123]. At this time it is believed that photoelectron spectroscopy (UPS and XPS) has the greatest utility for determining surface electronic structure and for relating electronic structure to surface atomic structure.

2.3.4 Summary of Measurement Needs

A large number of measurement methods (Appendix C) have been developed in the past ten years, primarily for applications in surface science. Many of these measurement techniques, together with other developments in experimental and theoretical surface science and newly developed concepts, are being increasingly applied in surface technology (e.g., failure analysis, quality control, and process development). At this time, however, there are still needs for new and improved measurement capabilities in both surface science and surface technology.

There is a widespread belief that many of the basic questions concerning surface processes and phenomena in catalysis, oxidation, corrosion, adhesion, lubrication, and wear can now be tackled [125-128]. This belief and the results that have been obtained to date are no doubt responsible for the tremendous recent growth of interest and work in surface science and technology [1-53]. The measurement tools now available and that have just been described have sufficient sensitivity and specificity to be usefully applied to prototype or model catalysis, corrosion, and adhesion systems; investigations of this type are in fact now being successfully carried out (section 3). Fundamental questions, such as those concerning bonding, specificity of catalytic reactions, reactivity of surfaces, kinetics, reaction paths, and intermediate species are being tackled.

The measurement techniques now in use need to be improved so that surface composition can be specified more exactly as a function of position, surface structure determined simply from LEED or other data, and surface electronic structure determined with greater reliability than at present. The sensitivity

of the surface-composition methods needs to be improved to detect dopants and impurities in semiconductor devices. Also, new measurement methods need to be developed so that catalytic and corrosion reactions can be studied at higher pressures and on "real" surfaces. Techniques are required to adequately characterize the small particles used as catalysts (with diameters of about 20 Å), and other surfaces with large amounts of disorder and defects. If sufficient conceptual advances can be made with the present or improved measurements techniques, it could be possible, for example, to engineer improved catalysts with greater selectivity, efficiency, and longevity for particular reactions. New techniques are also required to characterize the size and shape of pollutant particles and the reactions that occur on them. Special techniques need to be developed in the continuing quest for improved materials and processes (e.g., semiconductor devices of greater reliability and surfaces modified by ion implantation to have greater corrosion resistance).

The existing techniques for the determination of surface composition are being widely applied in surface technology (section 3.1). These techniques need to be further developed so that quantitative surface analyses of different types can be made with known accuracy. Specifically, reference data (section 2.2.3) concerning materials, instrumentation and the measurement process, reference materials (section 2.2.4), and procedures to make reliable and useful measurements need to be developed. Specific needs are itemized in section 4.2.3.1. As new techniques of potential are originated, it is anticipated that there will be similar needs for reference data, materials, and methodology.

2.4 Dissemination and Enforcement Network

2.4.1 Central Standards Laboratories

Programs concerned with certain types of surface measurements exist at the National Physical Laboratory in Great Britain, at the Electrotechnical Laboratory in Japan, and at the National Bureau of Standards. At present, the organizational infrastructure of this part of the National Measurement System (section 2.2) is not well developed; a national dissemination and enforcement network does not exist in the U.S. nor is there significant international activity in this area. This situation is expected to change in the near future as a result of the rapid growth of surface science and technology, the inauguration of ASTM committees on catalysts and on surface analysis, and as a result of NBS programs dealing with surface measurements.

2.4.2 State and Local Offices of Weights and Measures

There is no relationship now between NBS and any state or local office of weights and measures concerning measurement of surface properties nor is any such relationship anticipated in the near future.

2.4.3 Standards and Testing Laboratories and Services

Many of the manufacturers of surface instrumentation (section 2.2.2.2) offer analytical services that make use of their own instruments. In addition, other companies offer analyses of surfaces based on x-ray photoelectron spectroscopy, Auger-electron spectroscopy, secondary-ion mass spectroscopy, and ion-scattering spectroscopy.

2.4.4 Regulatory Agencies

There are not believed to be any regulatory agencies now concerned with the measurement of surface properties.

2.5 Direct Measurements Transactions Matrix

2.5.1 Analysis of Suppliers and Users

Table 2.4 gives a listing of the major suppliers and users of instrumentation, measurement techniques, measurement methodology, reference data, measurement concepts and analytical services for the measurement of surface properties, as discussed earlier in this chapter. The first column shows the major categories of suppliers while the second column gives examples or components of the major suppliers to indicate their scope. These suppliers provide a variety of measurement services, as indicated in the third column. It should be emphasized that the measurement suppliers (and users) do not form a cohesive unit with a well-defined pattern of activity amongst all members of the category. That is, individual members of a category may well supply different services at different times.

Figure 2.2 is an input-output direct-measurements transactions matrix for the measurement of surface properties. This matrix shows the nature of the transactions, according to the key at the bottom of the figure, between suppliers and users of measurement services in this portion of the National Measurement System.

Table 2.4. Major suppliers of instrumentation, measurement techniques, measurement methodology, reference data, measurement concepts and analytical services for the measurement of surface properties. Column 1 indicates the major categories of suppliers, column 2 shows examples or components of the categories to define their scope, and column 3 indicates the type of measurement service provided (A = reference data, B = measurement concepts, C = instrumentation and measurement techniques, D = measurement methodology, E = analytical services). The first column also shows the appropriate standard Industrial Classification (SIC) codes from the 1972 manual.

Supplier	Components	Measurement Service
(1) Knowledge Community (SIC Codes 2721, 2731 8221, 8621, 8922)	Scientific Organizations Academic Institutions Professional Societies Scientific and Technical Journals	A,B,C,D
(2) Documentary Standards Organizations (SIC Code 8621)	ASTM	A,D
(3) Instrumentation Industry (SIC Codes 3811 and 3823)	Manufacturers of Instruments	A,B,C,D
(4) NBS (SIC Code 9611)	Institute for Basic Standards Institute for Materials Research Institute for Applied Technology	A,B,C,D
(5) Testing Laboratories (SIC Code 7391 and 7397	Instrument Manufacturers Analytical Service Laboratories R and D Laboratories	A,B,C,D,E
(6) Department of Defense (SIC Code 9711)	e.g., Naval Research Laboratory Naval Weapons Center Naval Electronics Laboratory Air Force (CRL, WPAFB) Night Vision Laboratory Picatinny Arsenal	A,B,C,D
(7) Other Federal Government (SIC Codes 9611 and 9661)	e.g., Energy Research and Development Administration Contractors (e.g., Sandia Laboratories, Oak Ridge National Laboratory, Argonne National Laboratory) National Aeronautics and Space Administration	A,B,C,D
(8) Semiconductor Industry (SIC Codes 3641, 3661, 3662, 3673, 3674, 3573, 3699)	Manufacturers of semiconductor devices, computer components, lamps, special vacuum tubes, communication equipment, office equipment	A,B,C,D
(9) Chemical Industry (SIC Codes 2819, 2821, 2823, 2824, 2843, 2891 3861)	Manufacturers of plastics, films, fibers, composites, elastomers, adhesives, catalysts, photographic materials	A,B,C,D
(10) Petroleum Industry (SIC Code 2911)	Development of catalysts, production of petroleum products	A,B,C,D
(11) Metallurgical Industry (SIC Codes 3312, 3353 3411, 3711, 3721, 3724)	Manufacturers of ferrous and nonferrous metal products Automobile Manufacturers Aircraft Manufacturers	A,B,C,D

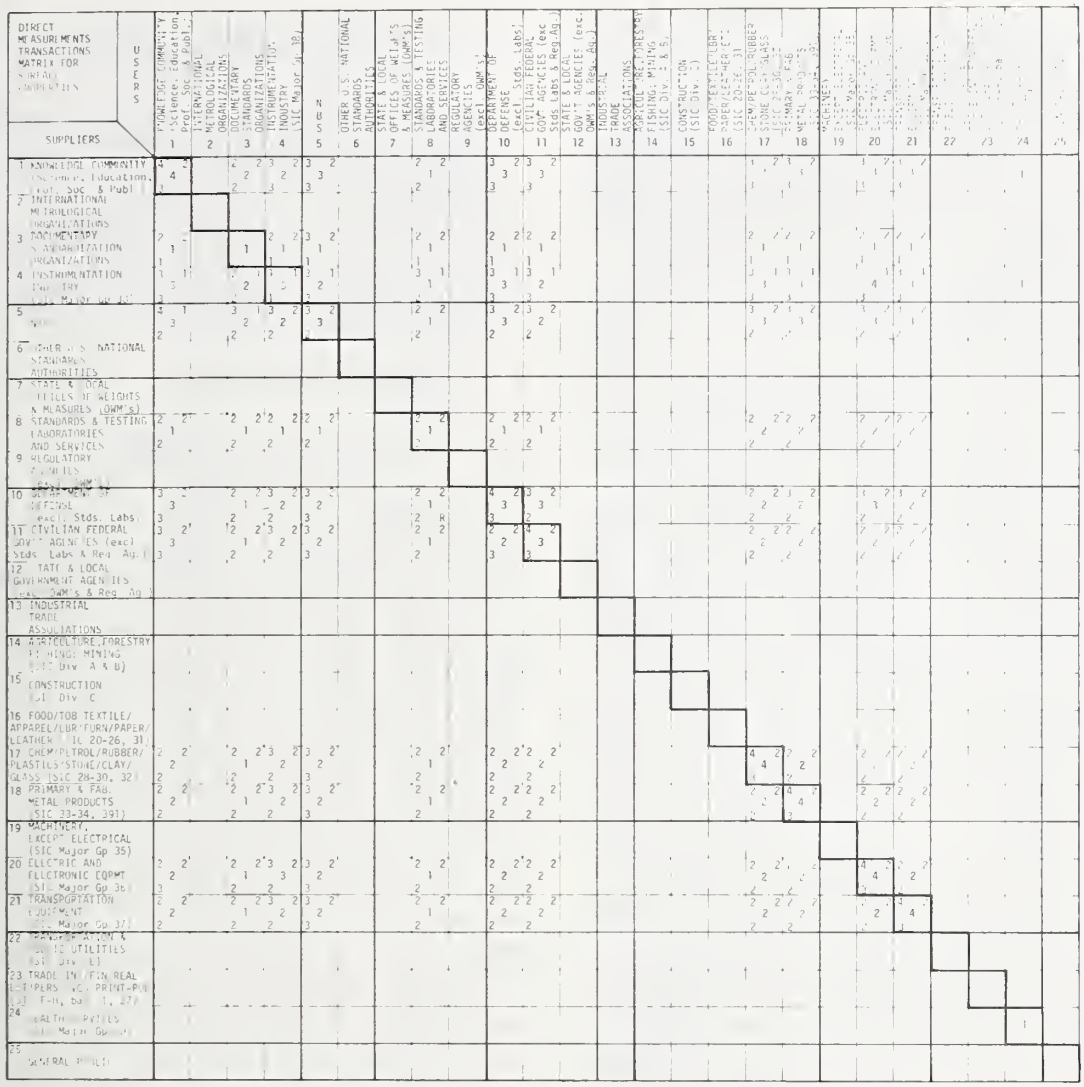
DIRECT MEASUREMENTS TRANSACTIONS MATRIX FOR SURFACE PROPERTIES
USERS
SUPPLIERS
1 KNOWLEDGE COMMUNITY (Science, Education, Prof. Soc & Publ)
2 INTERNATIONAL METROLOGICAL ORGANIZATIONS
3 DOCUMENTARY STANDARDIZATION ORGANIZATIONS
4 INSTRUMENTATION (SIC Major Gp 38)
5 OTHER U.S. NATIONAL STANDARDS AUTHORITIES
6 OTHER U.S. NATIONAL STANDARDS AUTHORITIES
7 STATE & LOCAL OFFICES OF WEIGHTS & MEASURES (OWM's)
8 STANDARDS & TESTING LABORATORIES AND SERVICES
9 REGULATORY AGENCIES (OWM & Reg. Ag.)
10 DEPARTMENT OF DEFENSE (excl. Stds. Labs)
11 CIVILIAN FEDERAL GOVT AGENCIES (exc Stds Labs & Reg Ag.)
12 STATE & LOCAL GOVERNMENT AGENCIES (exc. OWMs & Reg. Ag.)
13 INDUSTRIAL TRADE ASSOCIATIONS
14 AGRICULTURE, FORESTRY FISHING, MINING (SIC Div A & B)
15 CONSTRUCTION (SIC Div C)
16 FOOD/TOB TEXTILE/ APPAREL/LUR/FURN/PAPER/ LEATHER (SIC 20-26, 31)
17 CHEM/PETROL/RUBBER/ PLASTICS/STONE/CLAY/ GLASS (SIC 28-30, 32)
18 PRIMARY & FAB METAL PRODUCTS (SIC 33-34, 391)
19 MACHINERY, EXCEPT ELECTRICAL (SIC Major Gp 35)
20 ELECTRIC AND ELECTRONIC EQPMT (SIC Major Gp 36)
21 TRANSPORTATION EQUIPMENT (SIC Major Gp 37)
22 TRANSPORTATION & PUBLIC UTILITIES (SIC Div E)
23 TRADE (WHOLESALE & RETAIL) (SIC Div F-H, but excl. 27)
24 HEALTH SERVICES (SIC Major Gp 80)
25 GENERAL PUBLIC
C. Importance
1 = Minor
2 = Moderate
3 = Large
4 = Major
D. Adequacy: Amount of Improvements Required
0 = None
1 = Minor
2 = Moderate
3 = Large
4 = Major
USER
C
D
SUPPLIER
A
B
B. Rate of Change
N = Declining
0 = Stable
2 = Growing
4 = Explosive
A. Magnitude
0 = Trivial
1 = Minor
2 = Moderate
3 = Large
4 = Major

Figure 2.2. Input-output direct-measurements transactions matrix for the measurement of surface properties.

The central figure in each intersection box is intended to be a measure of the magnitude of the transaction, taking into account the amount of transfer of measurement and other information, economic magnitude, and the degree of measurement-intensiveness. In general, each supplier provides a different mixture of measurement services (column 3 of table 2.3) to each user so that the central digits in each box are at best semiquantitative estimates and in many cases meaningful intercomparisons cannot be made from box to box.

The figure in the bottom left-hand corner of each box is a measure of the rate of change (growth) of the transaction, while the number in the top left-hand corner is a measure of the importance, significance or criticality of the transaction, independent of its magnitude. The digit in the top right-hand corner of each box is a measure of the adequacy or inadequacy of the measurement transaction. In nearly all boxes, the latter digit has been coded 2 to indicate that nearly all measurement services are being performed at the current state-of-the-art although most users desire improvements in accuracy and precision, greater specificity and sensitvity, and lower cost, as discussed earlier. All digits in the figure must be regarded as subjective estimates of factors which are difficult to define precisely and determine objectively. Nevertheless, the estimates provide a coarse summary of the information given earlier in this chapter concerning the technical infrastructure, measurement capability, and measurement needs of this part of the measurement system and of the information to be presented in chapters 3 and 4 concerning the applications and impact of the measurements and the role of NBS, respectively.

2.5.2 Highlights re Major Users

The major user categories of surface measurements are (a) academic institutions, (b) government laboratories, and (c) industrial laboratories in the semiconductor, chemical, petroleum, and metallurgical industries. The types of measurements being made in these laboratories will be discussed in section 3.1.

3. IMPACT, STATUS, AND TRENDS OF MEASUREMENT SYSTEM

A survey of the more important methods of surface characterization was given in chapter 2. In this chapter, we will describe how the measurements are used, give estimates of the costs and economic benefits of the measurements, discuss the adequacy of the measurements, and give estimates of the future growth of measurement applications and measurement needs.

3.1 Impact of Measurements

3.1.1 Functional, Technological, and Scientific Applications

The diverse applications and impacts of surface science and technology have been referred to briefly in chapter 1 in excerpts from two recent reports prepared under the sponsorship of the National Academy of Sciences [1,2]. We will give here representative examples of applications of surface-characterization measurements that have been published in the literature, given to the author following personal inquiries to users of particular instruments, given to the author by instrument manufacturers, or given to J. T. Yates, Jr. in a related NBS survey. Some of this information was supplied on the understanding that particular individuals, laboratories, or companies would not be identified. To protect adequately such confidences and the related proprietary information, the sources of information presented in this section will not be given. It can be stated, however, that surface-characterization instruments are in active use in many laboratories of academic institutions, research foundations, government agencies, and large companies in the semiconductor, chemical, petroleum, and metallurgical industries.

3.1.1.1 Applications for Surface Science

Surface science is performed at universities, research foundations, government installations, and industrial laboratories. At this time, there appear to be two distinct but related thrusts in fundamental surface science.

First, considerable effort is being applied theoretically and experimentally to determine the relationships between surface composition, surface structure, and surface electronic structure. Experimental work of this type is often performed as far as possible on "ideal" surfaces (section 2.1) in order to compare measurements with

theoretical work. Research is also performed with "less ideal" or "real" surfaces, ranging from small particles, surfaces with various amounts and types of defects, to surfaces of metastable and amorphous materials. Many of the measurement techniques listed in table C.1 of Appendix C have been used for these measurements although the techniques listed in section 2.2.2.1 are utilized to a greater extent.

Second, a large amount of effort is being devoted to obtain a fundamental understanding of various electrical, optical, mechanical and chemical properties of the many different kinds of surfaces just described and of processes which occur on such surfaces. Specific problem areas are: adhesion, adsorption, diffusion from or to the bulk, catalysis, contacts, corrosion, crystal growth, epitaxy, evaporation, interface properties and reactions, nucleation, oxidation, radiation effects, segregation, surface conductivity, surface diffusion, surface-phase changes, surface reactions, surface thermodynamics, and thin-film growth, structure, and properties. Experimental and theoretical data are being obtained concurrently in many of these areas and are being related, where applicable, to the properties of the constituent or interacting materials or surfaces. This scientific work is motivated by needs for improved materials or processes and is usually closely coupled with related developmental programs. Applications of surface physics to the computer industry, for example, are described in a recent article by Branscomb [128].

Modern experimental surface science, as described above, must be performed with materials that are well characterized. The degree of characterization (section 2.1) may vary, depending on the nature of the work, but in most cases involves the surface composition and often surface structure. In other cases, particular properties (e.g., adsorption, oxidation, and reactivity) are being correlated with the electronic structure at the surface. Thus, part of the complexity (and cost) of surface science and technology is due to the many facilities that must be provided: surface generation and processing equipment, surface-characterization instrumentation, and components to measure the particular surface properties or processes of immediate concern.

3.1.1.2 Applications for Surface Technology

Applied research and development work on surfaces, surface properties, and surface processes is being performed at many government and industrial laboratories. We have found in this survey that the principal form of surface characterization is the determination of surface composition and that surface-composition information is obtained in most cases by Auger-electron spectroscopy (AES) or x-ray photoelectron spectroscopy (XPS), as could be inferred from table 2.2. We therefore show in this section specific examples of the applications of AES and XPS; similar examples have been found for ISS/SIMS (ion-scattering spectroscopy/secondary-ion mass-spectroscopy) instrumentation.

In the majority of present applications, surface-composition information is obtained for some relatively large area of a sample (depending on the particular measurement method), but it is believed that there will be an increasing demand for measurements of the distribution of particular elements or compounds in the plane of the surface. Information concerning the distribution with depth of particular species is desired for the majority of applications and is obtained by gradual sputtering of the sample, a process known also as "depth profiling" and "ion milling."

Measurements of surface structure and surface electronic structure are performed at some laboratories in order to relate these parameters to other desired surface properties (e.g., reactivity, photocathode response, stability, oxidation, diffusion, electrical properties, etc.) for the development of new materials and processes.

3.1.1.2.1 Government Laboratories

The research and development laboratories of civilian agencies and the Department of Defense have widely different missions and activities. There are, however, many surface-related, analytical, and developmental programs at many installations despite the diversity of objectives (e.g., space materials, energy programs, environmental applications, and defense). To illustrate this diversity, we give in table 3.1 examples of applications and uses of AES and XPS at eleven different laboratories; for some of the larger laboratories, the list of applications is almost certainly incomplete.

Table 3.1. Applications of Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) in twelve government laboratories.

Laboratory	Application
(1)	Migration of sodium ions in silicon dioxide under ion bombardment; segregation of impurities at grain boundary interfaces; fracture and embrittlement; oxidation protection; activation and poisoning of thermionic cathodes; correlation of infrared reflectance for various materials with surface composition; rocket engine catalysts (AES)
(2)	Hydrogen permeation, hydriding, and gettering processes; development of surfaces with increased corrosion resistance; role of surface composition on adhesive bonding and electroplating; poisoning of catalysts; relationship of catalytic activity and surface morphology to crystallography, composition and electronic structure; electrical contact studies; diffusion and surface segregation in thin films; electrochemistry at thin solid films (AES, XPS)
(3)	Improvement of reliability of equipment and components: corrosion problems and problems in semiconductor devices; contamination on electrical contacts; lubrication, cleaning and adhesion (AES, XPS)
(4)	Detection and analysis of protein functional-group modification (XPS)
(5)	Identify nitrogen and sulfur compounds in particulate soots: trace nature of surface reactions on atmospheric pollutants (XPS)
(6)	Material transfer in metal-polymer bearing systems (AES)
(7)	Electronic structure of metal hydrides; development of superconducting materials to operate at higher temperatures (XPS, AES)
(8)	Detection of different modes of sulfur (pyritic, sulfate, organic) in raw coal (XPS)
(9)	Oxidation, corrosion, and diffusion measurements (AES)
(10)	Role of surface contamination in damage of lenses, mirrors, and windows used with high-power lasers (AES)
(11)	Development and characterization of photocathodes (AES)
(12)	Role of first-wall contaminants on Tokamak performance (AES)

3.1.1.2.2 Semiconductor Industry

A more uniform pattern of applications, is found in the semiconductor industry where AES in particular is extensively used; SIMS is used in applications requiring higher sensitivity [129]. There are now three principal areas of application [4,30]:

(1) Process and Device Development. There is a continuing demand for new devices with improved performance or properties. New classes of materials are being developed as are new methods of fabrication and processing [128-130]. In addition, there is an increasing trend to microminiaturization and greater complexity of devices.

(2) Process Control. AES is frequently used to solve a variety of processing and production problems such as:

(a) identification of stains, remnants of a previous processing step, corrosion products, compounds formed at interfaces by diffusion, and dopants and contaminants in semiconductors at various stages of processing;

(b) analysis of failures of lead bonding, hermetic seals, and metallization adherence; and

(c) establishment of effective cleaning procedures. In these applications, decisions are often made by comparing an Auger spectrum from the sample of interest with one from a sample known to be satisfactory; that is, relative analyses are made on a given instrument.

(3) Failure Analysis. Devices of increasing density and complexity and of smaller size (microminiaturization) are being developed, but this trend has led to severe problems of reliability and yield. Typical yields of MOS/LSI devices, for example, are 5 to 8% of final assemblies.

Failure rates can be alarmingly high [131, 132], whereas reliability is crucial in large-scale civilian applications and in defense and space applications. In a recent analysis [132], 39% of device failures were attributed to surface-related defects and 18% of failures were attributed to metallization, oxide and bond defects. Many of these failures are caused by problems at surfaces or interfaces in the fabrication and processing of devices, such as residual contamination, adsorption of impurities, differential solubility, diffusion, void formation, electromigration, film dewetting, modification of surface electronic properties, and localized surface defects (e.g., dislocations, excessive roughness, and steps) [131,133]. The poor yields often found in the manufacture of complex LSI devices can be attributed to inadequate quality control during device manufacture; in particular, surface contamination during processing has been identified as a critical problem [132].

3.1.1.2.3 Chemical Industry

Table 3.2 shows examples of the applications of AES and XPS in the laboratories of six large chemical companies. A common objective in all of these laboratories was the development of improved catalysts.

3.1.1.2.4 Petroleum Industry

Table 3.3 shows examples of applications of AES and XPS in laboratories of seven large petroleum companies. The development and evaluation of process catalysts is again a common feature of all laboratories.

3.1.1.2.5 Metallurgical Industry

Table 3.4 shows examples of applications of AES and XPS in the laboratories of nine metallurgical companies (including automobile manufacturers). The applications here range from corrosion measurements and the development of protective coatings to failure analysis, diffusion measurements, segregation effects, fatigue, joining, wear and embrittlement.

Table 3.2. Applications of Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) in six chemical-industry laboratories.

Laboratory	Applications
(1)	Heterogeneous catalysis and properties of catalysts; relation of surface properties of fibers, plastics, and composites to adhesion and optical qualities; corrosion studies (XPS)
(2)	Development of improved process catalysts (greater selectivity, increased activity, lower cost); relation of catalytic activity to structural defects; adhesion phenomena: analysis of elastomers and substrates; role of surface composition on composite bond strengths; development of new alloys with lower corrosion rates, and longer process-container lines based on measurements of formation and breakdown of thin oxide films; interaction of surfaces with processing environments; technical problems of polymer films; process cleaning and wettability: surface adhesion (XPS, AES)
(3)	Development of improved catalysts; reactions at fuel-cell electrodes; corrosion measurements (XPS, AES)
(4)	Study of catalysis by metal particles (AES, XPS)
(5)	Development of improved catalysts for manufacture of chemicals and plastics; failure analysis and process development (AES)
(6)	Development of improved catalysts: correlation of catalytic activity with surface chemical species; acceptance testing of catalysts prior to use; elucidation of structure of complex organic molecules with N or S heteroatoms; detection of trace impurities with electrochemical enrichment; migration of ions following irradiation: changes of surface composition; treatment of catalysts to stabilize physical properties in working environment; analysis of surface coatings on particles in pigments (XPS)

Table 3.3. Applications of Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) in seven petroleum-industry laboratories.

Laboratory	Applications
(1)	Improvement of catalysts in chemical process applications (XPS)
(2)	Mechanisms of catalysis, and role of catalyst preparation and structure; development of new catalysts and catalytic processes; catalyst evaluation; corrosion on metal surfaces; wear phenomena; characterization of metals, plastics, and composites (XPS)
(3)	Surface species identification on active catalysts for petroleum refining or petrochemical processes; role of hydrogenating/dehydrogenating promoters on catalyst surfaces; types of solid acids on catalyst surfaces; surface species in corrosion, wear and fracture (XPS)
(4)	Characterization of surface composition and morphology on catalyst surfaces, including poisons and promoters; passivation of metal surfaces against corrosion; bonding of fibers; bonding of plastics; lubrication and wear (XPS)
(5)	Catalyst evaluation and synthesis (XPS, AES)
(6)	Catalyst evaluation and development; stability and regenerability of catalysts (XPS, AES)
(7)	Elucidation of active catalyst sites and their optimization and stabilization; improvement of catalyst activity and selectivity; role of catalyst support; effect of impurities on electronic states of the catalyst; role of dispersion in metal, alloy, and other catalysts (XPS, AES)

Table 3.4. Applications of Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) in nine metallurgical-industry laboratories.

Laboratory	Applications
(1)	Failure analysis and quality control in laboratory of steel company (AES)
(2)	Surface composition of powders and materials to be used for fuel cells; diffusion and segregation of impurities in alloys; grain-boundary phenomena in alloys; alloy foils; manufacturing problems: pickling, residuals of cleaning, bonding problems in welds (AES).
(3)	Poisoning of catalytic converter in automobiles; optimization of catalytic converter; corrosion and wear of surfaces at high temperatures; coverage of solid-state lubricants; surface reactions of exhaust gases in exhaust system and control of gas composition (AES)
(4)	Adherence and blistering of coatings; failure analysis; pickling rates; optimization of surface treatments to improve bonding of fibers in composites; temper embrittlement; coatings to reduce eddy current losses in transformer steels (AES)
(5)	Catalytic reactions and materials in auto emission control; catalytic activity as a function of alloy surface composition; elimination of poisons on catalyst surfaces; analysis of surface layers (coatings on glass or chrome, catalysts, oxides that affect joining, corrosion films, corrosion-protection coatings, phosphating, and painting of surfaces); impurities at internal interfaces (grain boundaries in steels and ceramics, fiber-matrix interfaces); development of processes for wear-resistant coatings and decorative coatings (AES)
(6)	Surface reactions and nature of films that form on alloy surfaces during processing; affect of surface films on welding, brazing, lubrication, wear, adhesion, electrical contact, resistance, radiation, durability (AES)
(7)	Dependence of durability of anodic films on surface composition for different preparation conditions; strength and durability of adhesive joints and the relationship to surface composition; development of production line tests to characterize surface and near-surface composition of adherends; develop passivating processes to improve resistance to corrosion, erosion, and stress-corrosion cracking and to give improved thermal and optical properties (AES, XPS)
(8)	Understanding of catalytic mechanisms and development of improved catalysts; electronic structure of surface defects on small particles; bond strengths of plated layers and of adhesive bonds; corrosion measurements (XPS, AES)
(9)	Correlation of hardness and corrosion resistance of steels with surface composition (AES, XPS)

3.1.1.2.6 Other Industries

Table 3.5 shows examples of applications of the use of AES and XPS in the laboratories of ten companies engaged in a variety of manufacturing industries ranging from electronic instrumentation and equipment, communications equipment, business machines, and glass products.

3.1.1.3 Summary of Applications

We have shown here many applications of surface-characterization measurements in surface science and surface technology. The most common form of surface characterization is a qualitative determination of surface composition, often as a function of position. Surface-composition data is now being

Table 3.5. Miscellaneous industrial applications of Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) in ten laboratories of manufacturing industries.

Laboratory	Applications
(1)	Quality control and failure analysis of incandescent lamps and lamp materials; process evaluation; mirrors: surface contaminants; phosphor coatings (AES, XPS)
(2)	Identify surface composition and corrosion products or reactor fuel pellets; diffusion studies of impurities in cladding; corrosion of pipes (AES)
(3)	Surface analysis of organic and molecular solids; process development for thin-film devices (AES, XPS)
(4)	Determination of average particle size for dispersed catalysts (XPS)
(5)	Lead monolayer lubrication in machining of steels: reduction of tool wear (AES)
(6)	Quality of films and interfacial bonds in compound device technology (AES)
(7)	Studies of catalytic reactions by transition metals and perovskite oxides; design of catalysts for chemical synthesis, energy conversion, and pollution abatement; passivation of surfaces; thin-film nucleation and growth, including epitaxy; characterization of semiconductor and insulator surfaces and interfaces; passivation of surfaces; development and fabrication of semiconductor devices and precision resistors, capacitors, and conductors; electronic structure of metal alloy and semiconductor materials; diffusion of species in semiconductor devices (AES, XPS)
(8)	Analysis of impurities and contaminants on semiconductor devices; phosphor screen analysis; product and device development (e.g., photocathodes) (AES)
(9)	Electronic properties of metal and semiconductor surfaces and of interfaces; diffusion measurements; surface reactions; catalytic decomposition; surface chemistry involving organics; corrosion chemistry; growth of oxide layers; radiation chemistry; development of new materials with special properties (XPS, AES)
(10)	Role of surface composition on strength and durability of glasses: vaporization and migration during fabrication (AES, XPS)

obtained by Auger-electron spectroscopy, x-ray photoelectron spectroscopy, and ion-scattering spectroscopy/secondary-ion mass spectroscopy (table 2.3). As pointed out in section 2.3, these measurement techniques have the ability to detect surface species with a sensitivity much greater than that available with other techniques. Although commercial instrumentation based on these new techniques has only been available for a short time, it is being used for a large number of applications in many industries. The industrial applications vary from problem-solving in analytical laboratories (e.g., failure analysis) to process and product development, process evaluation and process control. Examples of these applications have been described in a number of recent articles [134-143].

3.1.2 Economic Impacts - Costs and Benefits

We have estimated in section 2.2.2.2 that the total sales of surface-characterization instrumentation to date (i.e., within the past ten years) is about $70M and that the current sales volume is about $10M per year. About two-thirds of this instrumentation has been purchased by U.S. customers at an estimated cost of $7M per year. We assume that 500 instruments (LEED, AES, XPS, ISS/SIMS, and IMMA) are currently in use in the U.S. (table 2.3) and that each is operated by a scientist or engineer and a technician at a cost of $75K per year (combined salary and overhead). The labor cost of making the surface-characterization measurements is thus about $37M per year. The total spending for capital equipment and labor for these

measurements is then about $44M per year. This total does not include the costs of "homemade" or noncommercial instrumentation developed for use of other measurement methods (Appendix C), the associated labor cost for their operation, and the costs of additional ancillary equipment (e.g., residual gas analyzers, digital-data recording and processing systems, etc.). The total spending for surface-characterization measurements is therefore believed to be about $50M per year.

The benefits of surface-characterization measurements, economic and otherwise, cannot be usefully quantified at present as they involve government programs (e.g., defense and energy), the short-term and long-term benefits of scientific developments, work of a proprietary nature (e.g., development of improved catalysts), and a diversity of applications (for which there could be more than a single factor leading to the benefit). We can, however, give a qualitative assessment of benefits for the following categories.

(1) Surface Science. The benefits here are non-quantifiable in that one cannot readily attach a particular monetary value to a particular piece of scientific knowledge. There have been substantial developments in surface science in the past decade, as evidenced by the amount of activity and the scientific achievements noted in recent articles and reviews [1-53,128]. These developments have led to a greater fundamental understanding of surfaces, surface properties, and surface processes which have promoted most of the recent advances in surface technology. The scientific developments have also led to the production and utilization of new types of instrumentation that have unique sensitivity for the detection and solution of surface-related problems.

(2) Surface Analyses. A large fraction of the surface-analysis equipment (e.g., AES, XPS, ISS/SIMS) in industrial laboratories is used for general-purpose analytical or service work, particularly for failure analysis [27,28,30,129,133-143]. In addition, the instrument manufacturers and a number of private analytical laboratories perform analytical services on a fee-for-service basis.

It seems clear that the cost of these analytical measurements must have at least a corresponding economic benefit. Furthermore, the surface-analysis instrumentation discussed here has unrivalled sensitivity for the detection of surface contaminants and products; this instrumentation therefore has a unique capability for solving problems associated with or localized to a surface.

Although a single surface-analysis instrument costs typically $50-100K (table 2.3), one industrial user of AES equipment remarked to the author that "the instrument paid for itself in one week." That is, the cost of a production-line failure for even short periods of time can be appreciably greater than the cost of diagnostic analytical measurements.

(3) Surface Technology. As pointed out in section 3.1.1.2, surface-characterization equipment is used for the development of new or improved processes and materials for a variety of applications. Again, it can be reasonably assumed that the unique measurement capabilities of this equipment are generally being used to the economic advantage of the user; the nature and magnitude of the economic advantages can be inferred from the examples of application given in section 3.1.1.2.

Some individuals, in responding to requests for information on the nature of their surface-characterization measurements, specifically indicated that their activities involved proprietary products, materials or processes. According to them, their surface-characterization measurements were either of economic value to their company or of national benefit (in the case of a defense program).

One application, namely catalysis and the development of improved catalysts, stands out by its frequency in the responses made for information for this report. Haensel and Burwell [144] point out that catalysts play a major role in the production of goods worth more than $100 billion a year. Even slight improvements in the efficiency, selectivity, stability, and life of a catalyst can have considerable economic impact. Already, it is known that XPS has been used for acceptance testing of industrial catalysts prior to use, thus avoiding the expense of installation and unsatisfactory operation (in this case, a saving of several million dollars) [143]. Also, catalytic activity is being correlated with the surface composition of binary alloys (determined by AES) [126].

Another important area of impact is corrosion and the determination of the integrity and efficacy of anticorrosion coatings. It is known that AES is being used for quality control, by a buyer and a seller, of galvanized coatings on steel used for canning of food products. In another case, AES was used to determine the cause of paint blistering on the steel seats of a stadium, a multimillion dollar problem. Precipitates on ceramic surfaces and the material localized at corrosion pits have

been detected with a scanning Auger-electron microscope.

In the semiconductor industry, intermaterial diffusion (and device failure) is retarded by the deposition of intermediate layers; the significance and extent of diffusion was revealed by AES. Improved negative electron-affinity devices with many applications are being developed with the aid of AES.

(4) Government Programs. The surface-characterization measurements made in government laboratories benefit defense, energy, space, and environmental programs, as noted in section 3.1.1.2.1.

More general benefits of surface science and surface technology are discussed in the next section.

3.1.3 Social, Human, Man-on-the-Street Impacts

We have up to this point given examples of specific surface-measurement activities and programs at many laboratories. In some cases, the objectives of the programs were very clear while in others it could only be assumed that the program objectives were of value to the particular organization.

To give a clearer picture of the relevance and impact of surface-characterization measurements, surface properties and surface processes, we show in table 3.6 selected portions of the report "Materials and Man's Needs" sponsored by the National Academy of Sciences [145(a)]. The panel that prepared this report solicited the views of many experts on current needs in applied materials research and engineering. Table 3.6 gives a selection of the needs rated as "very high priority" or "high priority" that relate to surface properties and processes in nine major areas of public concern and societal need: (1) communications, computers, and control; (2) consumer goods; (3) defense and space; (4) energy; (5) environmental quality; (6) health services; (7) housing and other construction; (8) production equipment; and (9) transportation equipment. Clearly other measurement techniques than those discussed in this report will be required to develop improved materials, products, or processes for the various specific areas of applications. It is obvious, however, from this table and the specific examples of surface measurements and applications given earlier in this chapter that surface-characterization measurements are now having and will continue to have a considerable impact on programs and policies of major public concern.

3.2 Status and Trends of the System

Information concerning the current status of surface science, surface technology, and of surface-related measurements has been presented and discussed in several earlier sections of this report. In chapter 1, we quoted from two recent National Academy of Sciences reports that give independent assessments of the significance of surface science and the importance and relevance of surface technology. Advances in surface science and technology depend on reliable methods of surface characterization. The types of surface characterization were described in section 2.1 and the more important methods in section 2.2.2. The status of present methods of surface characterization was summarized in section 2.3 together with the more pressing needs for improved measurements; detailed needs are given in section 4.2.3.1. Information concerning the interactions amongst suppliers and users of surface-measurement services was given in section 2.5 while the impact of surface-related measurements was described in section 3.1.

We have pointed out in chapter 2.2.2.2 substantial growth (about 25% per year) of sales of surface-characterization instruments manufactured in the U.S.; the current sales volume is about $10M per year. This substantial growth rate is clearly related to a number of factors, amongst them, the establishment of public and private goals, the growing awareness that the recently developed measurement capability with previously unattainable surface sensitivity can be successfully applied to a wide range of practical problems and to a wide range of research and development work, and the belief among scientists and engineers that new concepts and measurement methods can be developed to extend present knowledge of surface processes and to provide other forms of surface characterization.

Table 3.6. Impact Areas of Applied Research and Engineering that involve surface properties, process, or measurements, selected from the recent National Academy of Sciences report "Materials and Man's Needs" [145].

---

(1) Communications, Computer, and Control

(a) Properties

Electrical: memories; solid-state circuitry, large-scale integration, display devices, Josephson devices, charge-coupled devices; miniaturization; reliability

Atomic structure: perfection; quality of crystals; surface effects; electromigration; ion implantation

Microstructure: defects in III-IV and II-VI semiconductors; defects in crystals; films and epitaxy; interface imperfections; electromigration; yields; metallization

Optical: optical properties; displays, solid-state lasers; optical communications; optical storage

Dielectric: surface effects at semiconductor/insulator interfaces; encapsulation; substrates

(b) Materials

Elemental and Compound Semiconductors: for electronic circuits; large-scale integration; displays; semiconductor memory; variable bandgap

Thin films: large-scale integration; control of metallization; thin-film memories; thin-film integrated optical devices; epitaxy; perfection of thin films

Ceramics: substrates, oxide layers, dielectrics; integrated optics; encapsulation; laser windows

Glasses and Amorphous Materials: optical transmission; integrated optics; laser windows; radiation-hand switches; glass for passivation

Inorganic, Nonmetallic Elements and Compounds: electro-optic microelectronics; displays; modulators; detectors

(c) Processes

Vapor and Electrodeposition, Epitaxy: yield and processing of large-scale integrated circuits; thin-film quality; epitaxy: greater miniaturization; control of metallization

Chemical: corrosion; compatibility in environment; contacts; connectors; doping; distribution of dopants; etching

Extraction, Purification, Refining: purification; synthesis; characterization

Synthesis and Polymerization: encapsulants; conducting adhesives; coatings; seals

Radiation Treatment: ion implantation; radiation damage

Plating and Coating: encapsulation; environmental protection

Table 3.6 (continued)

(2) Consumer Goods

(a) Materials

Plastics: stronger plastics; wear resistance; less brittleness; nonflammable plastics; impact-resistant plastics; biodegradable plastics;

Adhesives, Coatings, Finishes, Seals: Resistant polymers and rubbers; corrosion protection; enamels; hot-water tank coatings; self-cleaning coatings for ranges; reduce permeability of packaging films; bonding; fastening

(b) Processes

Plastics Extrusion and Moldings: reinforced plastic; composites; colloid properties; improved fibers

Synthesis and Polymerization: composite processing; biodegradable polymers; improved cross-linking; molecular architecture for special properties; improve fiber strength by controlling molecular orientation

(3) Defense and Space

(a) Properties

Mechanical and Acoustic: mechanical properties of composites; high-temperature materials; fatigue; corrosion fatigue; crack propagation; high-temperature fatigue; creep resistance; fracture toughness; impact resistance; fatigue resistance; undersea equipment; materials for pressure hulls

Microstructure: dispersion hardening; microstructural stability; corrosion pitting; uniformity of mechanical properties; radiation-resistant materials; hydrogen compatibility

(b) Materials

Composites: composites for ship construction; structural designs for composites; improved fracture toughness of composites; fatigue-resistant composites; dispersion-hardened alloys; reliability of composites

Adhesives, Coatings, Finishes, Seals: high-temperature coatings; fabrication of metal-nonmetal systems; integrity of polymer adhesives; degradation of adhesive bonds; antifouling coatings for ships; coatings to reduce corrosion; low drag and low contamination paints; room-temperature curing adhesives; thermal-control coatings; ablation materials; cements; sealants for deep-sea equipment

Joining: welding of titanium; weldable aluminum alloys; welding of dispersion-hardened alloys; joining of composites; adhesion mechanisms; seals for undersea repeaters

Testing and Nondestructive Testing: failure analysis; service life; failure prediction; nondestructive testing for welds

(4) Energy

(a) Properties

Chemical: batteries; higher energy density; improved electrodes; lower weight; longer life; catalysts for batteries; new container materials for batteries; corrosion of cables, of heat exchangers, of turbine blades; radiation effects on corrosion; high-temperature corrosion

Table 3.6 (continued)

Atomic Structure: solid-state electrolytes; hydrogen embrittlement; superconducting materials for power transmission

Microstructure: Radiation resistance; swelling; void formation; blistering; stability under high neutron fluxes; radiation-hard control equipment

Thermodynamic: combustion efficiency; thermoelectric power converters; magnetohydrodynamic conversion systems; electrohydrodynamic conversion systems

Mechanical and Acoustical: high-temperature materials for reactors, both for fuel containers and converters; lightweight conductors; high-temperature alloys for turbines; high-temperature bearings; creep; fracture toughness; high strength; toughness; notch sensitivity; fracture propagation in pipeline materials

(b) Materials

Ceramics: high-temperature materials for burners; for plasma containment; high-voltage insulators; ceramics for turbine blades

(c) Processes

Testing and Nondestructive Testing: failure criteria; lifetime prediction; nondestructive testing of reactor components

(5) Environmental Quality

(a) Properties

Chemical: catalysts for automobile exhausts; pollution detection of control systems; improved, cleaner extraction processes; improved beneficiation of ores; recovery processes

Biological: handling corrosive, toxic, and dusty materials; biodegradable plastics

(b) Materials

Plastics: wear

(c) Processes

Extraction, Purification, Refining: improved extraction methods; improved incineration methods; control of pollution and environmental degradation caused by mining and extraction

(6) Health Services

(a) Properties

Chemical: corrosion of implants; microbial corrosion; stress corrosion

Biological: biological response to implants; biocompatibility; rejection; toxicity; immunological response

Microstructure: adhesion; prosthesis/tissue interface; adhesion between implants and tissue

Mechanical and Acoustical: artificial bone, teeth, tissue, membranes, and organs, better filling material for teeth; fatigue; wear; alloys for joints

Table 3.6 (continued)

(b) Materials

Plastics: membranes; artificial teeth; dental adhesives; artificial heart valves; encapsulants for implants; containers for blood

Prosthetic and Medical Materials: implants; artificial organs, bones, teeth, tissue and membranes; compatibility and biological response

Fibers and Textiles: membranes, fine wires, organ replacements

Rubbers: artificial organs, tissue, membranes

Composites: for implants; bone and tooth replacements; joints; pins

Organo- and Organometallic Compounds: prosthesis-tissue interface; adhesion between bone and tissue; for implants

(c) Processes

Synthesis and Polymerization: dental adhesives; compatibility; interface between tissue and prosthesis

Plastics Extrusion and Molding: precision forming; controlled porosity; artificial organs; heart valves; membranes

Testing and Nondestructive Testing: quality control; methods to evaluate compatibility; characterization of properties of implants

(7) Housing and Other Construction

(a) Properties

Chemical: corrosion; atmospheric degradation

(8) Production Equipment

(a) Materials

Ferrous Metals and Alloys: harder dies; better cutting tools; better saws; rust resistance

Nonferrous Structural Metals and Alloys: improved wear and fatigue properties

Lubricants, Oils, Solvents, Cleansers: tribology-lubricants; wear and abrasion resistance

(b) Processes

Testing and Nondestructive Testing: quality control; fatigue failures

(9) Transportation Equipment

(a) Properties

Mechanical and Acoustical: fatigue; crack propagation; temperature cycling; better bearings

Microstructure: super alloys for engines; corrosion resistance; stress corrosion

Chemical: corrosion resistance; stress corrosion; corrosion fatigue; high-temperature oxidation; catalytic converters for automotive exhaust

Table 3.6 (continued)

(b) Materials

Adhesives, Coatings, Finishes, Seals: Adhesives and sealants for aircraft; adhesives for automobile bodies, frames, and repairs; coatings for automobile mufflers; coatings for turbine blades; seals for gas turbines; seals for Wankel engines; refractory coatings

Lubricants, Oils, Solvent, Cleansers: wear, abrasion resistance

Ferrous Metals and Alloys: improved high-temperature properties; corrosion resistance

Nonferrous Structural Metals and Alloys: superalloys; high-temperature materials for turbine engines

Plastics: composites

Composites: develop composites for use in engine and bodies of automobiles and aircraft; joining metals

(c) Processes

Metal Deformation and Processing: nondestructive testing evaluation

Heat Treatment: improved strength; high-temperature properties

Material Removal: improved shaping methods

Joining: fasteners and bonding systems for aircraft and for automobiles; joining methods for composite materials

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At this point it is useful to recall that the expression and establishment of major "national goals" generally sets in motion a chain of organizational and technical responses. A typical chain could include the development and relationship of policies, organizational approaches, technical approaches, hardware needs, applied materials research, and basic materials research over the necessary and appropriate time scales. On this basis, one can appreciate how the high-priority needs listed in table 3.6 for improved materials, properties, or processes relate directly to the particular goals under which they are classified. Similar relationships exist in industry between corporate decisions (e.g., to enter a market) and appropriate research and development activities.

We believe that the following national goals or policies will stimulate or require continued growth in surface-measurement capability.

(1) Energy. The energy crisis is a complex matter of very high public concern that will require a large number of governmental, corporate, and individual actions for its alleviation and eventual solution (by Project Independence). Surface technology will be required in at least the following four areas of activity.

(a) Controlled Thermonuclear Reactors. Whatever the type of reactor that may eventually be developed as an alternate source of energy, there will be a significant problem in the design of the "first wall" that will be exposed to the hot plasma [146-148]. Radiation from the hot plasma will strike the surfaces of the first wall (and perhaps other components, such as diverters and limiters) and will cause wall damage and erosion and the release of gas and impurity atoms into the plasma, thereby affecting adversely the performance and efficiency of the device.

A study group of the American Physical Society has recently reported that [147] "surface effects in CTR devices are strongly influenced by impurities, by adsorbed surface films, and by surface topography. Scrupulous attention must be paid to these points in all investigations in this area." Surface analysis is therefore required to analyze the topmost layers of the wall surface in order to gauge the efficiency of initial cleaning operations and to identify

the nature of the equilibrium surface for other performance criteria (e.g., sputtering, diffusion, and wear) [148].

(b) Laser Fusion. Laser-induced fusion is another potential technique for energy generation. In addition to the "first wall" problems noted in (a) above, damage can occur to the optical components (mirrors, windows, etc.) Damage thresholds are now strongly limited by surface defects (roughness, morphology of films) and by surface impurities (contaminants introduced by fabrication and by surface treatments) [149-150].

(c) Liquefaction and Gasification of Coals. Improved catalysts (with the necessary efficiency, stability, selectivity, and cost) need to be developed to obtain liquid and gaseous synthetic fuels from coal [126, 151]. Quantitative surface analysis will enable improved catalysts to be scientifically engineered so that the desired reactions can be promoted and undesired components (ash, sulfur, nitrogen) removed [152-155]. Identification of the nature and measurements of the rates of specific surface (catalyzed) reactions are also required so that improved (e.g., alloy) catalysts can be designed.

(d) Hydrogen. Hydrogen has been proposed as a major source of energy in the future [156-157]. There are substantial surface problems in hydrogen storage (as hydrides), transport (due to hydrogen embrittlement), and efficient use (e.g., in fuel cells).

(2) Defense. Surface technology is required for the development of rocket-engine catalysts, laser optical components, oxidation and corrosion protection, night-vision devices, lubricants, microelectronic devices, avoidance of fracture and embrittlement, development of high-performance composite and other materials, ablation materials, adhesion and welding of materials, failure analysis, and nondestructive testing; see also table 3.6.

(3) Advanced Materials. Needs for advanced materials, as determined by a National Academy of Sciences panel, that require surface technology are shown in table 3.6. Similar needs have been highlighted in a recent series of articles on high-technology materials [158].

The prediction of the durability of building materials and components, for example, is becoming increasingly important with the rapidly growing interest in life-cycle benefit-cost analysis. Many building materials (e.g., concrete and paints) are composites in which internal interfaces have an important bearing on performance. In addition, surface characteristics are of vital importance in a wide range of building materials (e.g., adhesives, building-joint sealants, built-up roofing, electrical terminations, paints, and coatings) for which degradation occurs primarily by surface processes.

(4) Environment. Improved catalysts and control methods are required for automobile exhausts, power-station exhausts, and factory exhausts. Improved measurement methods for determining the surface composition of pollutant particles in the atmosphere (as a result of the discharges from fossil-fueled power plants) and for determining the nature and rate of chemical reactions on the surfaces of these particles are urgently required.

(5) Health and Safety. New bio-compatible and nondegradable materials are required for prostheses and implants (table 3.6). The development of such materials will require the use of surface-characterization measurements to assess corrosion rates in the body environment. It is anticipated that surface-measurement techniques will be developed to characterize lipid membranes and to determine how the transport of drugs and carcinogens through such membranes can be controlled.

(6) Productivity. Many industries are currently using surface-characterization instrumentation and surface technology to improve products, develop new products or to improve yield (section 3.1.1.2). It is believed, based on the present activity and the recent growth of activity, that this use of surface technology will continue and probably intensify. Specific major areas of development will probably include:

(a) the development of catalysts with improved performance (efficiency, stability, and selectivity) for existing and new processes in the petroleum and chemical industries;

(b) the development of improved coatings and processes that can better withstand corrosion and wear (e.g., by ion implantation [159]);

(c) the development of semiconductor devices, particularly large-scale integrated circuits, with greater yield and greater reliability;

(d) the development of new components (devices, memories, displays, optical systems) for improved performance in the communications and computer industries; and

(e) the development of metal products with improved strength and service life.

(7) Transportation. Needs for improved properties, materials, and processes in the automobile and aircraft manufacturing industries are shown in table 3.6.

In addition to the needs and developments described above, it is believed that the following factors will further stimulate growth in surface-measurement capability.

(8) Surface Science. The development of surface science has reached the point where the properties of "ideal" surfaces (section 2.1) can be measured with reasonable confidence (section 2.3) and related to modern theories of surfaces. It appears likely that new and improved measurement techniques and methodologies will be developed to characterize "real" surfaces. Developments are anticipated in the following areas:

(a) methods to determine the local atomic structure of real surfaces, perhaps from the angular distributions of photoelectrons or of excited ions (originating from chemisorbed species);

(b) characterization of small particles or clusters (diameters $\geq$ 10 Å) that are used as practical catalysts [17];

(c) methods, perhaps optical, to characterize surfaces in high-pressure environments (e.g., working catalysts) where electron-spectroscopic methods are unsuitable;

(d) solution of other basic problems limiting the performance of industrial catalysts [153];

(e) methods to develop and characterize ultra-thin-film and microminiaturized semiconductor devices;

(f) determination of the relationship of surface atomic structure and surface electronic structure for "ideal" and "real" surfaces to surface properties, such as reactivity, bonding, corrosion, durability, wear, and lubrication; and

(g) determination of biophysical properties at biological surfaces and interfaces.

(9) New Instrumentation. The commercial instrumentation now used for surface characterization (section 2.2.2) has directly evolved from previously established scientific and technical knowledge. It is anticipated that instrumentation with improved capabilities for surface characterization will likewise be developed in the future [160]; for example, the recent development of a photoelectron microscope for imaging biological surfaces has benefitted from earlier work on electron optics and surface physics and will probably stimulate new applications in biophysics [161].

(10) Quantification. Many present methods of surface characterization are qualitative rather than quantitative (section 2.3). Although qualitative determinations of surface composition have been extremely useful for the solution of practical problems (section 3.1), it seems intuitively clear that the various types of instrumentation will not be used to their full potential until the results of the measurements can be expressed in absolute terms with known uncertainty.

(11) Legal. As the system for the measurement of surface properties becomes better established (chapter 2), it is anticipated that reliable means for the determination of surface composition, for example, will be used to specify the prepared or working surface of a proprietary coating or product (e.g., catalyst). Similar surface measurements will likewise be used in the prosecution and defense of patent suits where surface properties are involved.

(12) General Analysis. As the unique sensitivity of instruments that determine surface composition becomes more widely known in the technical community, it seems likely that the instruments will be used to solve a wider range of problems than those discussed in section 3.1; that is, there is no evidence of "saturation" in the present range of applications. It is therefore thought likely that within a decade most major laboratories will have surface-characterization instruments routinely available for analytical work, much as electron microscopes, mass spectrometers, chromatographs, x-ray analyzers, and spectrophotometers are available and in common use now. It is also believed that the surface sensitivity of the instrumentation discussed here could be valuable in forensic applications.

4. SURVEY OF NBS SERVICES

NBS has many programs concerned with properties of surfaces or of the surface regions (of varying depths) of bulk matter. These programs range from surface finish measurements, electron probe microanalysis, blood protein-polymer interactions, surface reactions and catalysis, semiconductor surface and interface properties, to corrosion measurements in biological, marine, underground, and atmospheric environments. In this chapter we will describe almost exclusively NBS programs in the Surface and Electron Physics Section of the Institute for Basic Standards. There is considerable cross-fertilization in the programs of this section with those of the Surface Processes and Catalysis Section of the Institute for Materials Research, and reference will be made to the latter programs where appropriate and to a recent unpublished study and evaluation of measurement needs in heterogeneous catalysis by Dr. J. T. Yates, Jr. There is also a recently established program in the Semiconductor Characterization Section of the Institute for Applied Technology concerned with methods for analysis of semiconductor surfaces.

4.1 The Past

4.1.1 History of the Surface Physics Program

We describe here the initial background and past accomplishments of the surface physics program conducted in the Surface and Electron Physics Section, a section which has been in existence for only 3 years. The elements of the program, however, have their origins in the Electron Physics Section founded in 1948 with Dr. L. Marton as Chief. Although the personnel assigned to the Electron Physics Section have changed over the years and the programmatic objectives have changed substantially, a particular philosophy can be discerned in the section's operation. A significant fraction of the section's effort has always been devoted to improving the state-of-the-art of electron-optical devices which have been applied in turn to a wide variety of current measurement problems. Specifically, new and improved types of electron guns, electron monochromators, electron energy analyzers, and electron lenses have been developed together with new design principles and data and with procedures to ensure that electron-optical devices can be operated in a satisfactory way. Although it has only been in recent years that electron-spectroscopic devices have been intensively applied to surface-related problems, surface characteristics have always been pertinent to the development of electron-optical devices (e.g., development of improved cathodes, processing of photomultipliers, and treatment of surfaces to minimize work function variations or secondary-electron generation).

Figure 4.1 illustrates the programmatic trends since 1955. In that year, the largest effort was devoted to measurements of inelastic electron scattering in solids in order to determine the mechanisms of contrast in the electron microscope. An effort to develop a novel x-ray microscope led to the development of a field-emission electron source that subsequently was used in a commercial flash x-ray tube. This project might be considered the forerunner of the present surface-physics program. Two years later, a field-emission program was established as part of an NBS program to study free radicals. Later, in 1961, a new program was established to measure work functions of well-characterized single-crystal planes of metals by a field emission method. By this time, the program to measure inelastic interactions of electrons with solids had diminished in size and was concerned principally with bulk properties of solids and with applications in radiation physics. In 1970, the Electron Physics Section was disbanded. The surface and solid-state related programs were incorporated into the Far Ultraviolet Physics Section (where there was an existing uv surface photoemission program) while the program to measure inelastic electron interactions in gases was incorporated into a new Electron and Optical Physics Section. A further reorganization took place in 1973 when the surface-physics and electron-physics elements of these two sections were combined to form a new Surface and Electron Physics Section. At this time, increased effort was applied to surface-related measurement problems by internal reprogramming.

The general and specific accomplishments, to be described in sections 4.1.2 and 4.1.3, respectively, are those related to surface physics and must be viewed both in relation to the current measurement needs (as discussed previously in section 3.2) and with regard to the changing resources applied to these problem areas.

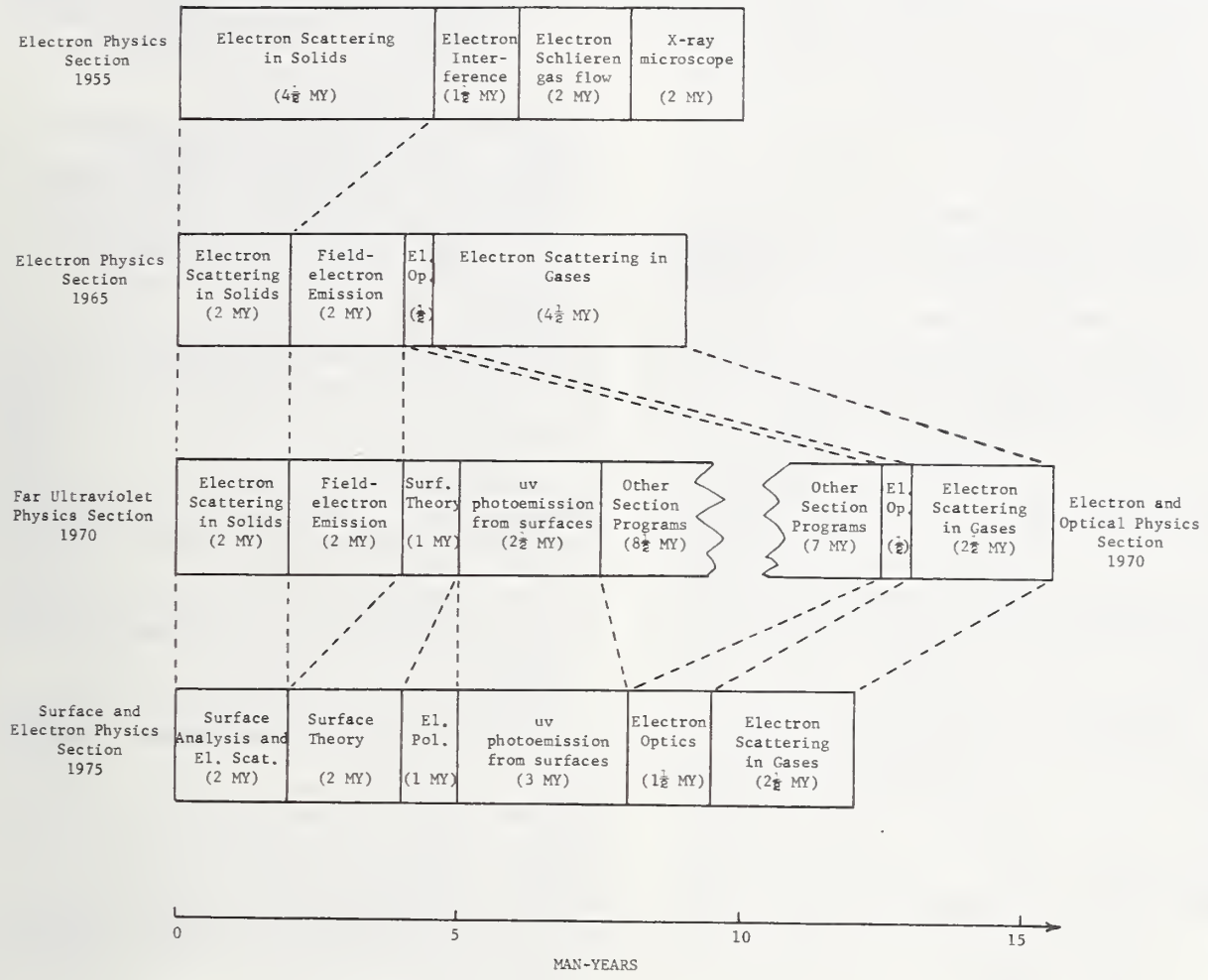
Electron Physics Section 1955
Electron Scattering in Solids (4½ MY)
Electron Interference (1½ MY)
Electron Schlieren gas flow (2 MY)
X-ray microscope (2 MY)
Electron Physics Section 1965
Electron Scattering in Solids (2 MY)
Field-electron Emission (2 MY)
El. Op. (½)
Electron Scattering in Gases (4½ MY)
Far Ultraviolet Physics Section 1970
Electron Scattering in Solids (2 MY)
Field-electron Emission (2 MY)
Surf. Theory (1 MY)
uv photoemission from surfaces (2½ MY)
Other Section Programs (8½ MY)
Other Section Programs (7 MY)
El. Op. (½)
Electron Scattering in Gases (2½ MY)
Electron and Optical Physics Section 1970
Surface and Electron Physics Section 1975
Surface Analysis and El. Scat. (2 MY)
Surface Theory (2 MY)
El. Pol. (1 MY)
uv photoemission from surfaces (3 MY)
Electron Optics (1½ MY)
Electron Scattering in Gases (2½ MY)
0
5
10
15
MAN-YEARS

Figure 4.1. Programmatic trends from the Electron Physics Section in 1955 to the Surface and Electron Physics Section of 1975 together with the corresponding number of full-time, permanent, professional employees. "El. Opt." denotes electron optics, "El. Pol." denotes electron polarization, and "El. Scat." denotes electron scattering in solids.

4.1.2 General Outputs of the Surface Physics Program

There have been several major programmatic directions taken in recent years whose general output will now be described.

(1) Field-electron emission measurement techniques and work-function data. From 1961 to 1974, improved analyzers were developed to measure the energy distributions of field-emitted electrons; these instruments were used to make reliable measurements of work functions of well-characterized single-crystal planes. The measurement of work-function changes was one of the few techniques available five to ten years ago to characterize surfaces. The instruments were used to detect and characterize single adsorbed atoms on a single-crystal plane, observe surface states on metals, describe the thermal field-emission process, and to obtain a surface density of electronic states.

(2) Photoelectron emission measurement techniques and data. In 1964 a program was initiated in the Far Ultraviolet Physics Section to measure photoelectric yields from clean and gas-covered metal surfaces in order to solve problems of plasma-wall interactions in fusion reactors and to describe the performance of photocathodes in space and other applications. In 1971, a new type of photoelectron analyzer was developed which has been used to observe and

monitor intermediate stages in the catalytic decomposition of ethylene on tungsten, to observe metal surface states, and to observe characteristic features identifying the species and bonding geometry of adsorbed gases on a metal surface.

(3) Surface Theory. Since 1968, theoretical effort supported jointly by the Institute for Basic Standards and the Institute for Materials Research has been directed to deducing the basic significance of surface spectroscopies and to stimulating new surface measurements. Significant accomplishments have been made in the areas of field emission, chemisorption, photoemission, and electron attenuation lengths in solids. This effort was expanded in 1974.

(4) Surface Analysis. A program was initiated in 1973 to enable quantitative surface analyses to be made by two popular electron-spectroscopic methods (AES and XPS). Measurements of electron attenuation lengths have been made by two new methods, and critical assessments made of attenuation-length and ionization cross-section data. Experimental tests have been made of simple models to describe the intensities measured in AES and XPS experiments.

(5) Electron Optics. Improved techniques have been developed to calculate the properties of electron lenses and to apply this data to the design of improved electron-optical systems such as high-resolution energy analyzers for field emission, Auger-electron spectroscopy and photoemission as well as other applications.

4.1.3 Specific Outputs of the Surface Physics Program

We show in table 4.1 some specific surface-related accomplishments of the Surface Physics Program that have occurred in the last five years. For convenience, we have subdivided these accomplishments into the five program areas described in section 4.1.2. In practice, however, there have been strong synergistic effects between various program elements at all times.

We have identified in the table both an accomplishment and a related impact. For the earlier accomplishments, the impacts have already occurred among the users to be described later in this chapter. For the more recent accomplishments, we have identified a potential impact based on our analysis of the status of measurements and/or the need for data in a particular field.

4.1.4 Cooperation between Surface Programs in the Institute for Basic Standards and the Institute for Materials Research

Modern surface science is an interdisciplinary endeavor involving chemistry, physics, and metallurgy. The need to have active cooperation between surface chemists and surface physicists has long been recognized at NBS, and active collaboration between these disciplines is an integral strength of the Surface Physics program in the Optical Physics Division and the Surface Finish Program in the Mechanics Division of the Institute for Basic Standards (IBS) and the Surface Chemistry program in the Physical Chemistry Division and the Corrosion program in the Metallurgy Division of the Institute for Materials Research (IMR). A theoretical physicist, Dr. J. W. Gadzuk, is working on the theory of surface phenomena of concern to both Institutes and his work is supported equally by IMR and by IBS. In addition, an informal joint IMR-IBS seminar meets weekly to discuss recent developments in surface science.

Staff members from the IMR and IBS surface groups have jointly sponsored a number of scientific conferences or lecture series at NBS. Among these are: the 14th Field Emission Symposium (1967), the lecture series "Introduction to Surface Properties" (1968), low-energy electron diffraction seminars (1970, 1971), the 31st Physical Electronics Conference (1971), and "The Electron Factor in Catalysis" Workshop (1975).

Surface science at NBS is widely recognized for its high quality. NBS is considered by many to be a premier institution in surface science and has been characterized as a national asset. The high external reputation of surface-science activities at NBS transcends disciplinary or organizational lines.

A joint research effort has been recently initiated between IMR and IBS. Ultraviolet photoelectron spectroscopy is being applied to heterogeneous catalytic reactions using a spectrometer developed and built by IBS. Personnel from both institutes are currently participating in this program, partially supported by the Office of Naval Research, and it is anticipated that NBS will make a significant impact by applying this technique to the identification and monitoring of intermediate species in catalytic reactions.

Table 4.1. Major Surface-Related Accomplishments of the Surface Physics Program from 1969 to 1974 and the nature of their impact.

Accomplishment	Impact
(1) Field-emission Program	
(a) Discovery of resonance tunneling of adsorbed atoms on field emitter.	A new technique for surface characterization in chemisorption experiments. Experiments confirmed virtual-bound-state model of chemisorption.
(b) Discovery of tunneling current from a metal surface state.	Existence of a surface state is a standard by which cleanliness of surface can be determined. Existence of the surface state has to be included in a complete description of surface electronic properties.
(c) Technique developed to measure work functions of single-crystal planes reliably.	New measurement techniques that can be applied to characterize surfaces.
(d) Observed high-energy "tails" on field-emission energy distributions.	Theory developed concurrently showed that this result was due to many-body processes.
(e) Observed smooth transition between field emission and thermionic emission as emitter temperature was raised.	Electron states between Fermi level and vacuum level can be observed and used to determine shape of potential barrier. Barrier transmission function used to interpret photo-field emission results.
(2) Photoemission Program	
(a) Observed catalytic decomposition of ethylene on tungsten and structure characteristic of C-C, C-H, and C-W bonds.	Powerful technique developed for monitoring catalytic reactions as intermediate species in complex reactions can be identified.
(b) Observed characteristic features for simple gases adsorbed on single-crystal faces of tungsten.	Spectra can be used as a library in later work to identify intermediate species in surface reactions. Microscopic data for atoms have been related to macroscopic properties of adsorbed layers.
(c) Observed surface state on metal surface for the first time.	Surface sensitivity of photoemission could be compared with that of field emission. Measure of cleanliness of a surface now exists for photoemission experiments.
(d) Observed angular dependence in uv photoelectron energy distributions.	Angular distribution for an adsorbed layer can be related (by theory) to the local bond geometry of the adsorbate on the surface.
(e) Photoelectron yield of tungsten changed when gases were adsorbed on surface (in vacuum ultraviolet region).	Showed sensitivity of photoyield to surface conditions. Showed likely variations in calibrations of photocathodes with and without exposure to gas.

Table 4.1 continued

(3) Surface Theory Program	
(a) Generalized theory of field emission developed including many-body effects, d-bands in transition metals and effects of chemisorbed atoms.	Used to provide unified theory of field emission. Many-body and band-structure effects can be determined. Differences in local density of states on different crystal planes of a metal can lead to different observed structures. Effects due to chemisorbed atoms can now be quantified.
(b) Junction-tunneling theory developed to account for effects of impurities in the barrier region and to relate tunneling to one-dimensional density of states.	Inadequacies of previous theories shown. Current-voltage characteristics can now be engineered by appropriate doping.
(c) Microscopic theory of alkali atom chemisorption on metals developed.	Used to interpret work-function change and desorption-energy experiments.
(d) Surface-molecule theory of chemisorption developed that includes chemical-orbital and solid-state band effects.	Results used for interpretation of experiments of adsorbed atoms on surfaces. Bond and band effects important in catalysis.
(e) Theory of photoemission developed for chemisorbed atoms and molecules.	Theory shows significant angular anisotropies in photoemission can be related to bonding.
(f) Theory of electronic relaxation developed for photoemission.	Theory explains observed line asymmetries and some satellites; intensities of the latter are needed for quantitative analyses by x-ray photoemission.
(g) Theory of inelastic electron scattering in thin films developed.	Results important for quantitative surface analyses by x-ray photoelectron spectroscopy and Auger-electron spectroscopy.
(h) Theory of optical absorption by adsorbed atoms developed.	Optical techniques will be valuable probes of surface conditions of catalysts in high-pressure environments.
(4) Quantitative Surface Analysis Program	
(a) Two new techniques for the measurement of attenuation lengths of low-energy electrons in solids developed.	Quantitative analyses of surfaces by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) are needed for many applications in industrial, government, and industrial laboratories (Chapter 3).
(b) Procedure developed to compute attenuation lengths.	
(c) Experimental and theoretical data on cross sections for ionization of inner-shell electrons evaluated.	
(d) Measured AES and XPS intensities, and compared with model predictions.	
(5) Electron Optics Program	
High-resolution improved state-of-the-art electron energy analyzers developed for field-emission, inelastic-electron-scattering, and photoemission measurements.	Improved measurement capabilities have led to new ways of characterizing surfaces and to the marketing of commercial instruments based on NBS designs.

4.1.5 Cooperation between Surface Programs in the Institute for Basic Standards and the Institute for Applied Technology

A program has recently been initiated in the Electronic Technology Division of the Institute for Applied Technology (IAT) to evaluate techniques currently in use for the determination of composition at surfaces, at interfaces, and throughout thin-film elements of semiconductor devices. This division is also interested in expediting the development and use of present and improved measurement techniques of established reliability. It is anticipated that there will be close ties in the future between the related IBS and IAT programs to develop standards and reference materials required by the semiconductor industry.

4.2 The present-scope of NBS Services

4.2.1 Description of NBS Services

Figure 4.1 shows programs of the Surface and Electron Physics Section in 1975. All of the experimental programs make use of state-of-the-art high-performance electron monochromators and/or electron energy analyzers that have been designed and developed as a result of the electron optics capability in the Section. An important feature of the work of the Section is the strong synergistic coupling between theory and experiment at all stages of every project.

One recently established program, not described earlier, is an effort to develop an efficient detector of electron spin polarization. Such a detector, in conjunction with a new source of monoenergetic spin-polarized electrons, would be used in electron-scattering experiments to identify exchange-scattering mechanisms and in diffraction experiments to determine the local atomic structure [99]. The detector is also expected to be used for measurements of the polarization of field-emitted electrons as a function of their energy. The effort on the electron-polarization project has increased since 1975 while the effort on the uv photoemission and electron scattering in gases projects has decreased.

Programs of the Surface and Electron Physics Section involve most of the following eleven operations:

(1) Identification of a measurement need (see also section 4.4);

(2) Development of a new or improved measurement method, instrument, or theory;

(3) Application of that measurement method or theory to a problem of current scientific or technical concern;

(4) Analysis of the data and results so obtained in relation to the body of scientific knowledge;

(5) Development of new concepts;

(6) Development of measurement procedures;

(7) Acquisition of measurement data for a sufficient number of materials and conditions to show the power or limitations of the measurement method or theory;

(8) Careful measurement of selected properties ("benchmark data") that can be used as tie points for data analysis, reference purposes (in relative measurements), and calibrations of instruments;

(9) Preparation of compilations or critical reviews of available measurement data and theories to meet the needs of those working in a particular field;

(10) Frequent evaluations of the current measurement needs in the particular technical community during the course of the program; and

(11) Frequent evaluations of technical progress and, with item (10), consideration of the need to redirect the objectives of the program.

The results of the various steps of the Section programs are disseminated to the scientific and technical community through presentations at meetings and scientific conferences (often sponsored by professional societies), technical reports (often to sponsors), articles in professional journals, published reviews, correspondence, and through consultations. In all of these activities, knowledge is disseminated. In many cases, new results of scientific significance and various types of reference data are distributed. In addition, measurement methodology, instrument performance, design data, instrument designs, and computer programs are disseminated. Personnel of the section have also been active in standardization activities, at first through a regional group of users of x-ray photoelectron spectrometers (the North-East ESCA Users' Group) and, more recently, through the ASTM Committee E-42 on Surface Analysis (section 2.2.1).

4.2.2 Users of NBS Services

The primary users of the measurement services provided by the NBS Surface and Electron Physics Section have been identified in section 2.5.1. These users benefit from the information generated at NBS and disseminated in the manner described above. Secondary and other users (of which the majority are other members of the same primary group) benefit in turn from the further dissemination of knowledge,

instruments, procedures, and data distributed by the primary users.

Surface science and surface technology are both relatively new, compared to many other branches of science and technology, and as some of the NBS surface-physics programs have only been established recently, a summary of "typical" applications of NBS services with the implication that these services have been utilized over many years would not be warranted. Nevertheless, an assessment of the use of NBS services can be gained from section 4.1.2 and table 4.1. Users of these results and developments would include the following:

(1) Designers of high-performance electron energy analyzers and other electron-optical instrumentation.

(2) Scientists who make use of the sensitivity of surface-state spectral features to surface contamination in order to determine the cleanliness of their surfaces.

(3) Scientists and technologists who need quantitative analyses of surfaces.

(4) Scientists working on the development of new or improved catalysts who need to detect and monitor the presence of different chemisorbed species.

(5) Scientists who wish to deduce the local atomic structure for atoms adsorbed on surfaces.

(6) Scientists and technologists who need reliable work-function data for well-characterized single-crystal planes.

(7) Scientists who wish to determine surface electronic structure by the various measurement techniques.

(8) Scientists and technologists who wish to know the efficiency of photocathodes on instruments used on space flights.

(9) Scientists who wish to use optical techniques to monitor the presence of adsorbates on surfaces.

(10) Scientists and technologists who make use of the instruments and measurement procedures developed at NBS.

(11) Scientists who make use of the reference data generated at NBS.

(12) Users of x-ray photoelectron spectrometers who need to know how the transmission of different instruments varies with electron energy.

4.2.3 Alternate Sources

4.2.3.1 Measurement Needs

Before discussing whether or not there exist alternate sources for the measurement services provided by NBS, it is desirable to summarize and review in this section the present needs for such services. A summary of the present measurement capability for the determination of surface composition, surface atomic structure, and surface electronic structure was given in section 2.3 together with a brief description of current measurement needs. The lack of documentary standards, adequate reference data, and of standard materials was pointed out in section 2.2. The overall need for improved measurement capability and improved measurement services is expected to grow based on the growth of surface science and surface technology in response to national needs and the other factors and trends described in section 3.2. Inasmuch as the most commonly used form of surface characterization is the determination of surface composition (section 3.1), we will summarize the most important measurement needs for this application in some detail.

4.2.3.1.1 Measurement Needs for the Determination of Surface Composition

The most common methods for the determination of surface composition are Auger-electron spectroscopy (AES) and, to a lesser extent, x-ray photoelectron spectroscopy (XPS). These two electron-spectroscopic methods of surface analysis have many common measurement needs.

(1) Initial excitation: ionization cross sections as a function of electron energy and the energy distribution of back-scattered electrons (AES); photoelectric cross sections in designated shells and subshells (XPS).

(2) Electron transport: electron attenuation lengths as a function of electron energy in different materials; anisotropies in crystals; matrix effects; modelling of electron transport; surface topography.

(3) Analyzer performance: transmission function; resolution; effect of modulation amplitude (AES); detector sensitivity.

(4) Geometry: relation of specimen crystallinity and orientation and possible anisotropy of electron transport to location and angular acceptance of analyzer.

(5) Measurement reliability: procedures to insure that representative regions of a sample are being measured; homogeneity of sample; transverse and depth variation of composition (resolution); procedures to insure meaningful calibration and operation of equipment.

(6) Radiation damage: electron and x-ray induced damage; desorption, decomposition, polymerization.

(7) Reference data: tabulations and reviews of line positions and line shapes

for elements and compounds in XPS and AES; role of chemical or local atomic environment.

(8) Standards: standard materials for calibration of energy, intensity, and depth-profile scales; standards for determination of measurement sensitivity.

(9) Procedures: procedures to determine composition from observed intensities.

(10) Sputter yields (for "depth-profile" measurements): data for elements, alloys, and compounds as function of ion type and ion energy; ion-induced dissociation and other damage; crater effects during analysis [7].

Amongst these needs, we have identified the following as the most pressing:

(1) Standards for calibration of the analyzer energy scale;

(2) Standards for the calibration of the analyzer intensity scale;

(3) Standards for depth profiling (thickness standards);

(4) Other surface standards (section 2.2.4);

(5) Reference spectra and line-position data;

(6) Attenuation-length data for electrons in solids;

(7) Inner-shell ionization cross-section data;

(8) Energy distribution and number of backscattered electrons (AES);

(9) Procedures to derive the surface composition from observed intensities;

(10) Sputtering yields of elements (and their variation with chemical environment) [7];

(11) Data for electron-beam or x-ray beam-induced damage to specimens.

The techniques of ion-scattering spectroscopy (ISS) and secondary-ion mass spectroscopy (SIMS) have the following measurement needs [23,25,26,76-84,162]:

(1) Primary beam: characterization of primary ion beam shape and current density.

(2) Scattering and ionization: ion scattering cross sections (ISS); neutralization effects; ionization efficiency (SIMS); matrix effects; role of molecular ions, multiply-charged ions, self-polymer ions, hydride ions, and primary ion-matrix molecular ions (SIMS); surface topography.

(3) Ion transport: Knock-on effects (SIMS); channeling in crystalline samples and orientation effects; energy distribution of secondary ions (SIMS).

(4) Analyzer performance: transmission function; resolution; detector sensitivity.

(5) Geometry: role of geometry in sensitivity and resolution; role of orientation of crystalline sample.

(6) Measurement reliability: procedures to insure reliability of measurement and homogeneity of sample; transverse and depth variation of composition (resolution); reliable operation of equipment.

(7) Ion damage: sputter yields and matrix effects; ion-induced damage to sample; crater effects during analysis [7].

(8) Reference data: tabulations and reviews of ISS and SIMS data for elements and compounds.

(9) Standards: standard materials (thin-film, insulator, and alloy standards).

(10) Procedures: procedures to obtain composition data from observed intensities.

4.2.3.1.2 Measurement Needs for the Determination of Surface Atomic Structure

Methods for the determination of surface atomic structure by low-energy electron diffraction (LEED) are still being developed. The differences between observed and computed intensities are still large enough to suggest that either the experimental data have been obtained from inadequately characterized samples, the theoretical models are not sufficiently accurate or complete, or the derived structure data may not be as accurate as believed. The most satisfactory methods of LEED data analysis are rather complex and costly (in computer time), and there is a need for the development of simpler procedures of acceptable accuracy.

As LEED only gives information on the surface atomic structure of ordered single-crystal surfaces, there is a pressing need for the development of other methods for the determination of local atomic structure on less ideal surfaces, as pointed out in section 2.3.

4.2.3.1.3 Measurement Needs for the Determination of Surface Electronic Structure

The theory of the "measurement process" for most methods of determining surface electronic structure is still not fully developed. As a result, the advantages and limitations of particular measurement techniques have only become apparent through extensive intercomparisons of experimental data. Improved measurement methods that give more direct information on surface electronic structure need to be developed both for single-crystal and less ideal surfaces. In view of the complexity of the relevant theory, there is a need for the continued empirical evaluation of the many

present (Appendix C) and anticipated measurement techniques.

4.2.3.1.4 Measurement Needs for Other Surface Properties and Processes

Measurement of surface composition, atomic structure, and electronic structure are frequently made so that other surface properties and processes (e.g., reactivity) can be related to fundamental surface characteristics. It is therefore important that the techniques of surface characterization be compatible with other measurement or operational requirements but, in general, this has often not been possible. For example, a catalyst may have to operate in a high-pressure working environment (pressure greater than one atmosphere) whereas measurements of surface composition by Auger-electron spectroscopy, say, have to be made in an ultrahigh vacuum (pressure about 10^{-8} Pa) [163]. There is therefore need for the development of special measurement methods (e.g., optical techniques) that can be calibrated against Auger-electron spectroscopy at low pressures and used at high pressures. Methods of this type could also be used to determine whether the composition of a surface has changed on going from a high-pressure working environment to a low-pressure measurement environment. Special measurement methods likewise need to be developed for other applications and conditions (e.g., nondestructive testing of integrated circuits, surfaces of fuel-cell elements, surfaces of biological membranes, surfaces of highly dispersed catalysts, and surfaces of particulate pollutants in the atmosphere).

4.2.3.2 Sources of Measurement Services

Many members of the industries and organizations listed in figure 2.2 have developed or provided surface-characterization measurement services, as discussed in chapter 2 and indicated schematically in table 2.4. Many important contributions have been made by many individuals from industrial, government, and university laboratories to meet some of the measurement needs listed in section 4.2.3.1, particularly in the provision of reference data. These efforts, however, do not usually represent a significant part of the organizations' missions. Also, the results of such programs usually do not involve most of the eleven significant components of a successful measurement-service program listed in section 4.2.1 on account of various institutional, economic, or competitive constraints.

The need for an NBS role in supporting the Surface Properties section of the National Measurement system can be appreciated from the following quotations from letters received from the manufacturers of surface-analysis equipment and from industrial users of this equipment. These letters were received in response to requests for comments on the need (several years ago) for the then-proposed establishment of a NBS surface-analysis program and (later) on the specifics of the program.

"Most of our Auger spectrometers will be going into the analytical chemistry groups in the various companies and industries. The scientists in these groups are typically chemists with experience in the standard bulk chemical analysis techniques. The first question we always get when talking to these scientists concerning equipment sales is 'to what accuracy can you tell me the quantity of a species present on this surface.' At the present time we cannot be very confident or accurate with the quantitative analysis because of the lack of standard data."
(Instrument manufacturer, October 1971)

"... At the present time, the chemical interpretation of photoelectron spectra is often confused by little-understood surface effects occurring in a depth up to 100 Angstroms. In general, we do not understand or know the electron escape depths, the depth dependence of surface charging, the radiation-induced surface conductivity or the nature of the chemical compound at the surface of the sample. Methods for preparing samples of known surface composition have not been worked out. The effect of vacuum gases on the surface characteristics as exhibited by photoelectron spectra is not understood at all.... Matrix corrections for quantitative analysis by electron spectroscopy have not been worked out.

"Certainly our sales would increase if electron spectroscopy could be made quantitative. However, industry cannot afford to do the basic research required to establish this capability."
(Instrument manufacturer, October 1971)

"We feel that there is a need for NBS to begin a program to measure and compile data relevant to Auger and ESCA. This should be not only electron escape depth, ionization cross section, and surface induced damages as a function of energy, and material and surface preparation but also to establish standards for performance such as

1. Spectrometer Calibration - (a) stability, (b) accuracy, (c) resolution, (d) signal to background, (e) signal to noise, (f) signal level (intensity)
2. Relative line intensities
3. Charging effects
4. Standards.

There is a sufficient need for the data for NBS to be involved. The individual companies will never produce data that can readily be compared."
(Instrument manufacturer, November 1971)

"To summarize, I think it would be most helpful if the Bureau of Standards could participate in the evolution of electron spectroscopy. Much work remains to be done to make these techniques quantitative. The development of standard cross sections as a function of electron energy and of electron absorption for the emerging photoelectrons would be most helpful. The development of standardized methods of correcting for these matrix effects would be a significant contribution. I sincerely hope you are in a position to launch such a program."
(Instrument manufacturer, December 1971)

"I am very happy to see that you have initiated this program which I think can provide extremely useful information for the users of AES and XPS equipment, particularly with respect to quantitative analysis.

"From the user's point of view, there is another area which adds confusion to the quantitative capability of surface analysis techniques on practical surfaces, and this is the surface topography. Variation in surface topography can cause great differences in absolute sensitivity in a measurement technique such as Auger electron spectroscopy, and perhaps you may have some suggestions as to how to take this into account."
(Instrument manufacturer, June 1973)

"The factors which we find to be important in a practical sense, are the ones you have designated as (1) initial excitation, (2) electron transport or mean free paths for inelastic scattering of electrons. Analyzer performance, in the sense of the instrument's intensity response as a function of electron energy, is also a factor which must be accounted for."
(Instrument manufacturer, July 1973)

"... We are most enthusiastic about the (NBS) program and feel that it is important and desirable from both the user's and manufacturer's point of view. The problem with leaving this type of work to industry or equipment manufacturers is competitive pressure and economics.
(Instrument manufacturer, September 1973)

"Yes there is a real need for quantifying these measurement processes if one wants to do serious work. Those who will go into the more complicated systems approximating applied ones will be grateful for having a tool that will help them sort out the mess.

"Yes NBS should do this work. Why not us? Because we have enough to do to try to solve the energy problem. I think this is a classic case of the definition implied in spelling out NBS. Furthermore, many industries are hampered in a comparison effort by secrecy."
(Head of surface science group of a major petroleum company, December 1972)

"It is extremely important to quantify these measurement processes (XPS, AES) through such media as round-robin testing."
(Director of a Materials Science Laboratory of a catalyst manufacturer, January 1973)

"Our surface problems are in the fields of catalysis, adhesion, and corrosion. We feel that significant progress cannot be made in any of these areas without the 'new' surface techniques that you are speaking of.

"There is no question that there is a real need for quantifying these measurement processes. The state of the art is not quantitative as yet. While information can be gathered with present techniques, the methods are far from optimized.

"Industrial scientists are interested in information about specific materials and processes. They would indulge in standardization only occasionally.

"Any standardization of a measuring apparatus requires "known" samples. One role that NBS could play would be to standardize surface preparation techniques so that experiments can be systematically repeated in several laboratories.

"Comparison of spectra on different Auger and ESCA machines should also take account of variations in the excitation sources, different geometries for surface preparation in situ, etc. That is, more than just transmission functions need to be compared."

(Member of corporate research laboratory of a major automobile manufacturer, January 1973)

"In the Semiconductor industry, the role of surfaces on device properties has become of vital importance. We have been aware of this shift in emphasis from bulk to film to surfaces for some time. While monitoring progress in characterization techniques, it has become clear that the new surface techniques are not capable of generating quantitative results. One of the major reasons for this lack of quantitation is, of course, the lack of standards.

"One of the most useful surface techniques is Auger spectroscopy. This technique can characterize surfaces to a depth of 10 to 20 angstroms and when coupled with ion sputtering, can give in-depth composition analysis in 10-20 angstrom increments for several thousand angstroms. Unfortunately, all of the analytical data is at best semi-quantitative.

"It appears that the National Bureau of Standards should be actively involved in the generation of standards for surface analysis; particularly for Auger spectroscopy. These same standards could be used for photoelectron spectroscopy (PES, ESCA). As part of this standards development, the development of quantitative techniques would be essential."

(Director of Materials Characterization Laboratory of a major manufacturer of semiconductor devices, December 1975).

"In the past few years, having applied the Auger technique in semiconductor manufacturing methods and failure analysis, I felt an acute need for proper standards for surface characterization. Often the surface composition of a material is critically dependent on the manufacturing method and also on the manufacturer.

"Standards with accurately known impurity concentration and location in depth (such as ion-implanted species) would be very desirable from the viewpoint of determining the minimum detectable limits of each technique. Often the concentration derived from the electrical parameters such as resistivity, may not give the true surface concentration of an impurity. In such cases it would be desirable to have reference samples with accurately known concentration of impurities, in which one can have confidence rather than depending on the 'hand-waving' evident in the literature.

"There is also an acute need for thin film samples of accurately known thicknesses. Such samples will be of immense value in determining the depth-resolution and the sputter rates in the composition profile measurement using AES and ion sputtering.

"For those experimentalists who are primarily concerned with the application of AES in problem solving, the Auger spectra from elemental samples have been compiled (though not without minor errors) and made available commercially. However, this could not be said about the spectra from all inorganic compound materials. Often one has to search the vast literature for reference spectra and even then one may not find the relevant spectra. Compiling reference Auger spectra from all inorganic compounds might be a prohibitive task. Nevertheless, it will be of great value if such spectra from materials one usually encounters in the electronics industry were to be compiled and made available to the user. In this context, it will be further helpful to tabulate the 'chemical shifts' (if any) in these materials.

"I strongly feel that the NBS is the only establishment capable of playing a key role in providing standard samples and reference spectra, one may need in the proper characterization of a solid surface. I hope your laboratories will undertake the task, immense as it may be, of providing the necessary framework for and resolving the confusion in surface analysis."

(Member of technical staff of a major manufacturer of semiconductor devices, December 1975)

"From the discussions that occurred during our recent ASTM E-2.02 Subcommittee for Surface Analysis meeting and Subcommittee Task Group meetings, the unanswered questions concerning surface analysis certainly far outnumber the answered ones. It is the wish of each of our Task Groups - AES, ESCA, SIMS, ISS - to quantify the analytical measurements of these techniques. As you are aware, this requires in many cases the knowledge of parameters of fundamental nature as well as theoretical procedures for making use of the measured data. Standard materials and well-characterized surfaces are also needed.

"We understand that NBS has undertaken work to answer some of these questions and make certain necessary measurements. We heartily endorse this program as a valuable undertaking for all those in the field of surface analysis. We hope this program will be successful. Please keep us informed of your progress."

(Secretary of ASTM Subcommittee E-2.02 on Surface Analysis - now Committee E-42 on Surface Analysis, November 1975)

Present NBS programs have been selected to be responsive to the measurement needs listed in section 4.2.3.1 within limits set by available personnel and funding. Specifically, programs now exist for the quantification of surface analyses, for the determination of surface electronic structure, and the determination of surface atomic structure (by the diffraction of polarized electrons and through use of the theory of the angular distributions of photoemitted electrons), as indicated in sections 4.1 and 4.2. It is anticipated that new measurement methods for specific applications in science and technology (section 4.2.3.1.4) will continue to be developed at NBS in conjunction with the other elements (section 4.2.1) of our programs.

4.2.4 Funding Sources for NBS Services

As shown in figure 4.1, there are 8 full-time professional employees in the NBS Surface and Electron Physics Section (in 1975) devoted to surface-characterization programs. In addition, a significant fraction of the electron optics program (1½ employees) leads to improved surface-characterization instrumentation. These activities involve an expenditure of $411K (FY 75) of which $343K originates from directly appropriated NBS funds. The other $68K is received by contract from the Energy Research and Development Administration for measurements describing the interaction of electrons with solids.

4.2.5 Mechanism for Supplying Services

The results of NBS programs are disseminated by a variety of mechanisms:

(1) papers published in scientific and technical journals (see Appendix D);
(2) papers published in review journals (see Appendix D);
(3) papers presented at regional, national, and international scientific meetings;
(4) presentations at workshops;
(5) reports to sponsors;
(6) individual consultation;
(7) correspondence;
(8) participation in ASTM activities;
(9) distribution of computer programs;
(10) distribution of design data and mechanical drawings of NBS instruments;
(11) visits to manufacturers of surface-characterization instruments; and
(12) visits to university, government, and industrial laboratories.

In addition, members of the Surface and Electron Physics Section have attained positions of leadership in professional societies, have participated in the planning and organization of scientific conferences, and are frequently asked to referee manuscripts submitted to journals and to review proposals submitted for support to various government agencies.

4.3 Impact of NBS Services

The most significant recent NBS accomplishments have been listed in table 4.1 together with assessments of the corresponding impacts. These accomplishments have been disseminated by the methods indicated in section 4.2.5 and are being used by personnel in industrial, government, and university laboratories, as shown in section 4.2.2.

The impact of NBS work (and the esteem in which NBS personnel are held in the scientific and technical community) can be gauged from the extensive number of citations to NBS work in the published work of others (as listed in recent editions of the *Science Citation Index*) and from knowledge that NBS results and data are used frequently (often on a day-to-day basis) in many laboratories. NBS personnel are frequently invited to give talks at major national and international scientific conferences, to participate in international science programs (e.g., International Center for Theoretical Physics at Trieste, NATO Advanced Study Institutes),

and to serve on committees of professional societies (e.g., of the American Physical Society, the American Vacuum Society, the Physical Electronics Conference, and ASTM), and on review panels. On this basis, it is believed that NBS personnel have earned a high reputation for impact and effectiveness.

A listing of recent NBS publications, by the personnel associated with the programs shown in figure 4.1, is given in Appendix D.

4.3.1 Economic Impact of Major User Classes

The users of NBS measurement services are affiliated principally with manufacturers of surface-characterization instruments, government laboratories, university laboratories, and laboratories of the semiconductor, chemical, petroleum, and metallurgical industries (sections 2.5 and 3.1). These organizations are concerned with the advancement and application of fundamental knowledge, the development and sales of instruments to promote science and technology, the promotion of national defense and public welfare, and the development and marketing of a wide range of products that are directly and indirectly of benefit to the public (computers, communication equipment, lamps, plastics, adhesives, catalysts, petroleum products, automobiles, and aircraft), as pointed out in section 3.1. The significance of surface measurements and properties has also been emphasized in two recent reports sponsored by the National Academy of Sciences [1,2].

NBS programs have supported and promoted the development of surface science through the development of improved measurement methods and the provision of reliable reference data. Developments in surface science have led to the development of commercial surface-characterization instrumentation, to advances in the understanding of surface properties and processes, and to advances in surface technology. The recently established NBS program to quantify measurements of surface composition is now beginning to support surface technology.

4.3.2 Technological Impact of Services

The impact of surface-characterization measurements in science and technology has been discussed extensively in section 3.1 while the factors which will cause growth of surface-measurement capability in the future were described in section 3.2. The nature of the impact of NBS programs has been pointed out in sections 4.1 and 4.2.2.

4.3.3 Payoff from Changes in NBS Services

The reorganization in 1973 that led to the formation of the Surface and Electron Physics Section was the result of recognition by NBS management of the current and growing importance of surface science and surface technology; in some earlier years, the surface programs had been often regarded as subordinate to other priorities and programs. The recent reorganization has thus provided a new focus and visibility for surface-related measurements and surface-related problems. At the same time, some internal reprogramming led to the establishment of the surface-analysis program in response to the measurement needs that had become apparent to the staff over a period of several years. Recently, a new program has been initiated to develop an improved source and detector of polarized electrons that are expected to be used for many scientific and technical purposes.

4.4 Evaluation of NBS Program

The National Bureau of Standards has the authority [164] to undertake "the study and improvement of instruments and methods of measurement" for "the determination of physical constants and properties of materials when such data are of great importance to scientific or manufacturing interests and are not to be obtained of sufficient accuracy elsewhere."

Needs for NBS services in response to current measurement problems are determined from a variety of sources:

(1) Staff awareness of trends in science, technology, and of related matters of public concern (e.g., energy crisis, environment, defense, health, and safety, etc.);

(2) Staff attendance at scientific conferences;

(3) Staff visits to university, government, and industrial laboratories;

(4) Staff visits to manufacturers of surface-characterization instrumentation;

(5) Staff participation in meetings of ASTM committees;

(6) Individual contact with users of surface-characterization instrumentation;

(7) Examination of scientific and technical journals; and

(8) Suggestions made by external advisors (e.g., the Evaluation Panel of the NBS Optical Physics Division which previously has recommended strengthening and expanding the surface-measurements program).

Decisions to undertake and continue projects are based on the following considerations:

(1) Assessments of the magnitude of the need in relation to the corresponding impact and benefits (perhaps through an "issue study");

(2) Determination that similar work is not or is unlikely to be undertaken elsewhere (of the necessary quality);

(3) Determination of a likely time scale for the work;

(4) Availability of resources (personnel, funds, equipment); and

(5) Current policies of NBS management.

Present NBS surface-measurement programs are thus the product of continuing input and evaluation in response to the mandate expressed in the NBS enabling legislation. The success or adequacy of NBS programs is gauged by NBS management, NBS Evaluation Panels, and the reactions of the users of NBS services.

Previous and current NBS surface-measurement programs are distinguished by the following strengths:

(1) A creative and competent staff whose work is recognized nationally and internationally to be of high quality;

(2) An integrated program involving capability in instrument development and design, experiment, and theory;

(3) Existence of a measurement capability and expertise in the forefront of the field;

(4) Provision of a variety of services ranging from new instruments, reference data, data analyses, measurement procedures, analyses of the "measurement process" for various measurement methods, new concepts, and calculations of material properties; and

(5) Significant impact on existing measurement problems.

4.5 The Future

We would like to summarize here reasons for believing that NBS surface-measurement programs will be required in the future (that is, for at least the next five years).

(1) Surface science and surface technology are both growing in importance (chapters 1 and 3).

(2) Substantial measurement problems and needs now exist (sections 2.3.4 and 4.2.3.1).

(3) Manufacturers of surface-characterization instruments have requested NBS to provide measurement services that support use of these instruments. Proposed NBS programs of this type have been endorsed by both manufacturers and users.

(4) Applications for surface-characterization measurements are expected to increase (section 3.2).

Recommendations for NBS action are summarized in the next section.

5. SUMMARY AND CONCLUSIONS

We have presented an analysis of the state of the National Measurement System for the Measurement of Surface Properties. This part of the National Measurement System is distinguished principally by the fact that, as yet, there is *no* formal system of the type found in most other areas of physical measurement (as discussed in the other reports of this series).

We now give the principal findings and recommendations resulting from the present study.

(1) Surface science and surface technology are widely regarded as being "frontier" areas in which major scientific breakthroughs will occur and in which major improvements in materials and processes will occur (chapter 1). Most of the significant advances to date in surface science and the significant developments and applications of surface technology have occurred during the past ten years (chapters 1 and 3).

Present national goals for solution of the energy crisis, provision of an adequate defense capability, control of environmental pollution, increase of industrial productivity to improve the national economy, and the development of advanced materials for the automobile and aircraft industries and for improved individual health and safety will stimulate or require growth of surface-measurement capability (sections 3.1.3 and 3.2). Other factors which will stimulate growth in surface-measurement capability are projected developments in surface science, development of improved instrumentation, development of quantitative methods for surface characterization, legal needs, and anticipated growth in the applications of surface analysis (section 3.2).

The present growth of surface measurements has occurred in the absence of a formal measurement system (chapter 2). At this time, measurements are based on informal conventions rather than formal definitions (section 2.1). There is no established system of documentary specifications, and there is a complete lack of standards, standard procedures, and standard materials to support surface-related measurements (section 2.2). The extent of this problem has been recently realized and an ASTM Committee on Surface Analysis has been organized (section 2.2).

Recommendation 1. It is recommended that NBS support surface science and surface technology by establishing, through its own programs and through the stimulation of organizations such as the ASTM Committee E-42 on Surface Analysis, a satisfactory measurement system for surface properties.

(2) The large number of solid-surface properties that can be measured have been divided into two groups. The first group contains properties that are used to characterize a surface, such as surface composition, surface atomic structure, surface electronic structure, the nature and distribution of surface defects, surface topography, and the nature and area of exposed facets. The second group contains derived properties such as electrical properties, optical properties, adhesion, bonding, catalytic activity, plating, durability, corrosion, decoration, grain-boundary segregation, lubrication, and reactivity (section 2.1). Many of these latter properties and processes, of considerable scientific and technological significance, depend in detail on the composition, atomic structure, and electronic structure of the surface (section 3.1). Improved products and processes depend on the control, design, and measurement of these three surface characteristics (chapter 3).

(3) The principal form of surface characterization in use at the present time is the measurement of surface composition (section 2.2.2). Determinations of the distribution of particular chemical species across a surface and as a function of depth from the surface are frequently required (sections 2.1 and 3.1).

Other forms of surface characterization (e.g., nature and distribution of defects on a surface, the surface topography, and the nature and area of exposed facets) are expected to be required in the future for particular scientific and technical applications (sections 2.1 and 3.2).

(4) Most measurements of surface composition are performed by Auger-electron spectroscopy and, to a lesser extent, by x-ray photoelectron spectroscopy, ion-scattering spectroscopy and secondary-ion mass spectroscopy (section 2.2.2). The sales of these instruments are estimated to be $10M per year with a present growth rate of 20 to 30% per year (section 2.2.2.2). It is estimated that about 60% of the instruments to determine surface composition are in use in industrial laboratories, about 20% in Federal Government laboratories, and about 20% in university laboratories (section 2.2.2.2). These surface-analysis instruments are used routinely to solve a wide range of industrial problems in the semiconductor, chemical, petroleum, and metallurgical industries. The applications range from process and device development, process control, process evaluation to failure analysis (section 3.1.1.2). The same instruments are being used in Federal Government laboratories for many purposes, for example, in support of defense, space, energy, and environmental objectives (section 3.1.1.2.1). University laboratories frequently employ these instruments in order that investigators can relate fundamental surface properties to surface composition (section 3.1.1.1).

The cost of surface-characterization measurements is estimated to be about $50M per year (section 2.2.2.2). Data concerning specific economic benefits have been hard to isolate but the direct benefits to industrial laboratories, in particular, are believed to be substantially greater than the cost of the measurements (section 3.1.2).

Most measurements of surface composition are now qualitative rather than quantitative (section 2.3.1). Manufacturers and users of surface-analysis equipment have pointed out the need for the development of methods and the provision of reference data and reference materials so that quantitative analyses of surfaces with known accuracy can be obtained (sections 2.2, 2.3, and 4.2.3). These services cannot be provided on the necessary scale at the needed rate by instrument manufacturers and users on account of various institutional, economic, and competitive constraints (section 4.2.3.2). An NBS program to meet specific measurement needs has been strongly endorsed by instrument manufacturers and representative users (section 4.2.3).

Recommendation 2. It is recommended that NBS, through its own internal program and through cooperation with the ASTM Committee E-42 on Surface Analysis, develop methods and provide reference data and reference materials to enable surface analyses to be made with known accuracy using, initially, Auger-electron spectroscopy and x-ray photoelectron spectroscopy and, later, secondary-ion mass spectroscopy and ion-scattering spectroscopy.

(5) The surface atomic structure of ordered surfaces is now being determined by low-energy electron diffraction (section 2.3.2). A variety of other measurement techniques have been recently proposed for the determination of the local atomic structure of surfaces which do not necessarily have the long-range order needed to generate an electron diffraction pattern (section 2.3.2).

Recommendation 3. It is recommended that NBS explore and develop improved methods for the determination of the local atomic structure of surfaces.

(6) Many techniques are being used to determine surface electronic structure but considerable uncertainty remains in the proper interpretation of the measurement data (section 2.3.2).

Recommendation 4. It is recommended that NBS theoretical and experimental effort be directed to resolving the measurement problems in the determination of surface electronic structure.

(7) Most methods for the characterization of surfaces can be employed only in an ultrahigh vacuum environment and some of these methods can only be employed on relatively ideal (i.e., single-crystal) surfaces (section 2.3.4). There is a need for the development of improved measurement methods that will allow surfaces to be characterized at higher pressures and that will enable the composition and structure of disordered surfaces, highly dispersed catalysts, biological surfaces, and pollutant particles in the environment to be measured (sections 2.3.4 and 3.2). More sensitive measurement methods need to be developed to identify transient species on surfaces and the kinetics of reacting species (sections 2.3.4 and 3.2).

Recommendation 5. It is recommended that NBS develop improved measurement methods for the determination of the surface composition, atomic structure, and electronic structure of practical surfaces of significance in science and technology.

(8) Many of the present users of surface-characterization instruments do not have extensive experience in surface science or technology and have had difficulty in selecting instruments to meet their needs or in using these instruments satisfactorily (section 2.2.5). With the present rapid growth in surface science and technology, there is a continuing need for short courses and review articles that provide up-to-date evaluations of instruments, techniques, and methods of data analysis for specific types of applications (section 2.2.5).

Recommendation 6. It is recommended that NBS sponsor short courses and prepare status reports as needed to assist existing and potential users of surface instrumentation to select and apply instruments, methods, and techniques in order to efficiently solve current industrial measurement problems.

(9) NBS programs in surface physics have had considerable impact on the development of surface science through the development of new instruments and measurement methods, the observation of new surface properties and processes, the development of new theories and concepts, the provision of reference data, and the publication of data compilations and critical reviews (sections 4.1, 4.2, and Appendix D).

Until recently, the major goal of the NBS effort has been to support and promote surface science (sections 4.1 and 4.2). Surface technology has grown substantially within the last five years and NBS data has been widely used for many applications (sections 4.1, 4.2, and 4.3).

Many measurement problems exist in surface science and technology (sections 2.2, 2.3, 3.1.3, 3.2, and 4.2.3.1). Significant problems exist in determining the properties, particularly the relationships between particular physical characteristics such as composition and particular surface processes (such as corrosion, catalysis, adhesion, lubrication, and wear). The basic science needs to be developed so that surface properties can be understood from a fundamental point of view and so that surface science can be used to design improved products and processes (section 3.2).

Recommendation 7. It is recommended that NBS continue to support surface science and surface technology through the development of improved measurement methods, through theoretical and experimental programs designed to show the significant relationships between surface characteristics and surface properties and processes, and through the provision of reference data needed by the scientific and technical community.

Effective response to the foregoing recommendations should lead to the establishment of a satisfactory National Measurement System for the Measurement of Surface Properties.

APPENDIX A. METHODOLOGY OF THE STUDY

Information for this report was derived from a variety of sources, the most important being:

(1) background knowledge of the staff of the Surface and Electron Physics Section;

(2) supplementary reading of relevant recent journal articles, reviews, and books;

(3) presentations given at recent conferences and workshops on surface science and technology;

(4) conversations and correspondence with users of surface-characterization instruments;

(5) visits to or conversations with manufacturers of surface-characterization instruments;

(6) conversations with members of ASTM Subcommittee E2.02 (now Committee E-42) on Surface Analysis;

(7) letters sent to Dr. J. T. Yates, Jr., of NBS in response to inquiries for a companion study;

(8) examination of customer lists supplied by some manufacturers of surface-characterization instruments;

(9) phone calls to representative users of surface-characterization instruments (whose names were on manufacturers' customer lists); and

(10) comments and suggestions made by interested scientists.

The author is extremely grateful to the many people who provided help and information for this report and who made constructive suggestions to improve the first draft of the report.

APPENDIX B. SUMMARY OF RECENTLY-PUBLISHED BACKGROUND DOCUMENTS

1. Title: Characterization of Solid Surfaces
Edited by: P. F. Kane and G. B. Larrabee
Published: Plenum Press, New York, 1974 (670 pages)
Contains: 23 articles on different methods of surface characterization

W. C. McCrone: "Light Microscopy"
A. C. Hall: "Multiple-Beam Interferometry"
D. J. Whitehouse: "Stylus Techniques"
C. Laird: "Electron Microscopy"
O. Johari and A. V. Samudra: "Scanning Electron Microscopy"
P. F. Kane: "Field Ion Microscopy"
R. D. Dobrott: "X-ray Diffraction Methods"
D. M. MacArthur: "Electrochemical Techniques"
J. L. Seeley and R. K. Skogerboe: "Emission Spectrometry"
N. J. Harrick and K. H. Beckmann: "Internal Reflection Spectroscopy"
J. A. Keenan and G. B. Larrabee: "Radioisotope Techniques"
J. V. Gilfrich: "X-ray Fluorescence Analysis"
S. H. Hercules and D. M. Hercules: "Surface Characterization by Electron Spectroscopy for Chemical Analysis (ESCA)"
D. Hanemann: "Resonance Methods"
M. C. Hobson, Jr.: "Mossbauer Spectroscopy"
W. D. Mackintosh: "Rutherford Scattering"
T. B. Pierce: "Accelerator Microbeam Techniques"
G. A. Hutchins: "Electron Probe Microanalysis"
W. L. Baum: "X-ray Emission Fine Features"
C. C. Chang: "Analytical Auger Electron Spectroscopy"
J. M. McCrea: "Mass Spectrometry"
D. V. McCaughan and R. A. Kushner: "Impurity-Movement Problems in Analysis Methods using Particle Bombardment"
C. W. White, D. L. Simms, and N. H. Tolk: "Surface Composition by Analysis of Neutral and Ion Impact Radiation"

Comment: A useful up-to-date compilation of articles. Some of the articles describe techniques that are not surface-sensitive as defined in this report.

2. Title: Surface Science: Recent Progress and Perspectives
Edited by: T. S. Jayadevaiah and R. Vanselow
Published: CRC Critical Reviews in Solid State Sciences 4, Nos. 2 and 3, 1974 (426 pages)
Contains: Proceedings of the International Summer Institute in Surface Science, University of Wisconsin, Milwaukee, Wisconsin, August 27-31, 1973. Contains 21 articles on recent developments of surface science.

P. H. Emmett: "Fifty Years of Progress in Surface Science"
L. K. Runnels: "Surface Statistics"
D. Robertson and G. M. Pound: "Heterogeneous Nucleation and Film Growth"
G. Ehrlich: "Surface Self-Diffusion"
J. P. Hobson: "Physical Adsorption"
R. Gomer: "Some Aspects of the Theory of Chemisorption"
A. J. Bennett: "Some Electric Properties of Solid Surfaces"
F. C. Tompkins: "Heterogeneous Catalysis: Reactions of Simple Molecules at Metal Surfaces"
J. H. Sinfelt: "Heterogeneous Catalysis: Some Aspects of Catalysis by Metals"
A. N. Broers: "Recent Advances in Scanning Electron Microscopy of Surface Topography"
A. van Oostrom: "Surface Analysis by FIM and AP"
C. B. Duke: "Electron Solid Scattering"
J. C. Tracy and J. M. Burkstrand: "Recent Advances in Surface Characterization using LEED and Auger Electron Spectroscopy"
D. Lichtman: "Surface Characterization by Electron, Ion, Photon, and Surface Wave Induced Desorption"
R. Greenler: "The Use of Thermal Desorption, IR Spectroscopy, and Ellipsometry for Surface Analyses"
G. A. Somorjai and S. B. Brumbach: "The Interaction of Molecular Beams with Solid Surfaces"
D. R. Franke: "Surface States"
R. F. Greene: "Surface Electron Transport"
F. Stern: "Quantum Properties of Surface Space-charge Layers"
A. Many: "Relation between Physical and Chemical Processes on Semiconductor Surfaces"
C. B. Duke: "Future Perspectives in Surface Science"

3. Title: Proceedings of the Second International Conference on Solid Surfaces
Published: Japanese Journal of Applied Physics, Supplement 2, Part 2, 1974 (920 pages)
Contains: Proceedings of the International Conference held at Kyoto, Japan, on March 25-29, 1974. Sixteen invited and many other papers are published. The invited papers are:

E. W. Müller: "Atom-Probe Field Ion Microscopes and High-Field Surface Effects"
H. D. Hagstrum: "Some Topics concerning the Electronic Characterization of Solid Surfaces"
Y. Uemura: "Landau Levels and Electronic Properties of Semiconductor Interface"
M. Drechsler: "Crystal Shape Changes in Vacuum: Determination of Surface Quantities on Field Emitter Crystals without and with Adsorbed Layers"
T. N. Rhodin and J. E. Demuth: "Chemisorption on (001), (110), and (111) Nickel Surfaces"
R. Gomer: "Some Aspects of the CO-Tungsten System"
D. Haneman: "Review of EPR Investigations of Semiconductor Surfaces"
J. Horiuti: "Catalyzed Reactions by Solid Surfaces and Adsorption"
J. H. Block: "Field Ion Mass Spectrometry of Oxygen, Sulphur, and Selenium at Different Metal Surfaces"
J. Kistemaker and H. E. Roosendaal: "Fundamental Processes in Surface Erosion by Sputtering"
K. Kambe: "Theory of Low-Energy Electron Diffraction at Crystal Surfaces"
C. B. Duke: "Determination of the Structure of Solid Surfaces by Low-Energy Electron Diffraction"
V. Heine: "The Theory of Electrons at Surfaces"
R. L. Park, J. E. Houston, and G. E. Laramore: "Comparison of Many-Body Effects in Core level Surface Spectroscopies"
A. A. Maradudin: "Edge Modes"
W. E. W. Ludwig: "Theory of Surface Phonons in Diamond- and Zincblende-Lattices"

4. Title: Proceedings of the 21st National Symposium of the American Vacuum Society
Published: Journal of Vacuum Society and Technology 12, No. 1, January-February 1975 (594 pages)
Contains: Proceedings of the National Symposium held at Anaheim, California, on October 8-11, 1974. Contains many invited and contributed papers on a variety of topics pertaining to surface science, vacuum technology, vacuum metallurgy, and thin-film phenomena. Topics of the sessions relevant to this report are:

Welch Memorial Lecture: "The Development of Ion-Neutralization Spectroscopy" (H. D. Hagstrum)

Thin Film Symposium: Metallization
Insulating Films
Unique Properties
Film Growth and Characterization
Films for Energy Conversion

Surface Science Symposium: Interactions of Atoms with Surfaces
Structure of Chemisorbed Layers
Electronic Structure of Surfaces
Photoemission Studies
Chemisorption

Vacuum Science and Technology Symposium: Analytical Depth Profiling Techniques
Hydrogen-Metal Interactions
Ion-Material Interactions and Techniques

5. Title: The Solid-Vacuum Interface
Edited by: G. A. Bootsma and J. W. Geus
Published: Surface Science 47, No. 1, January 1975 (412 pages)
Contains: Proceedings of the Third Symposium on Surface Physics, University of Utrecht, The Netherlands, June 26-28, 1974. Many papers are published on the following topics: electron spectroscopy; alloy surfaces; chemisorption on metals; semiconductor surfaces; electron diffraction; nucleation and surface diffusion; ion scattering; secondary ion mass spectrometry; desorption studies.

6. Title: A Special Issue on Surface Physics
Published: Physics Today 28, No. 4, April 1975, pages 23 to 71 (April 1975)
Contains: Five articles on different aspects of surface physics.
J. R. Schrieffer and P. Soven: "Theory of the Electronic Structure"
P. J. Estrup: "The Geometry of Surface Layers"
D. E. Eastman and M. I. Nathan: "Photoelectron Spectroscopy"
R. L. Park: "Inner-shell Spectroscopy"
E. W. Plummer, J. W. Gadzuk, and D. R. Penn: "Vacuum-tunneling Spectroscopy"

7. Title: "Techniques for Elemental Composition Profiling in Thin Films"
By: J. W. Coburn and E. Kay
Published: CRC Critical Reviews in Solid State Sciences 4, No. 4, 561-590 (September 1974)
Contains: A good, up-to-date summary of the measurement techniques used for surface analysis, the techniques of depth profiling, and of the damage to surfaces by ion bombardment.

8. Title: Electron Spectroscopy
Edited by: R. Caudano and J. Verbist
Published: Journal of Electron Spectroscopy and Related Phenomena, Vol. 5, 1974 (1124 pages)
Contains: Proceedings of the International Conference on Electron Spectroscopy, Namur, Belgium, April 16-19, 1974. Contains many papers on instrumentation, techniques, photoelectron production cross sections, photoelectron spectra, theoretical models, surface studies, valence-band studies, and analytical applications of x-ray photoelectron spectroscopy.

9. Title: Surface Physics of Crystalline Materials
Edited by: J. M. Blakely Published:
Academic Press, New York, 1975
Contains: Ten articles on different topics of surface physics.
J. A. Strozier, Jr., D. W. Jepsen and F. Jona: "Surface Crystallography"
J. A. Appelbaum: "Electronic Structure of Solid Surfaces"
H. J. Leamy, G. H. Gilmer and K. A. Jackson: "Statistical Thermodynamics of Clean Surfaces"
J. M. Blakely and J. Shelton: "Equilibrium Adsorption and Segregation"
M. Henzler: "Electronic Transport at Surfaces"
H. P. Bonzel: "Transport of Matter at Surfaces"
J. W. Gadzuk: "Interactions of Atoms and Molecules with Surfaces"
R. L. Park: "Chemical Analysis of Surfaces"
M. Lagally: "Surface Vibrations"
D. Tabor: "Interactions between Surfaces: Adhesion and Friction"

10. Title: Aspects of the Study of Surfaces
Edited by: I. Prigogine and S. A. Rice
Published: Advances in Chemical Physics 27 (John Wiley and Sons, Inc., 1974) 633 pages
Contains: Five review articles on surface physics and surface chemistry.
C. B. Duke: "Determination of the Structure and Properties of Solid Surfaces by Electron Diffraction and Emission"
R. Gomer: "Electron Spectroscopy of Chemisorption on Metals"
E. N. Economou and K. L. Ngai: "Surface Plasma Oscillations and Related Surface Effects in Solids"
K. L. Kliewer and R. Fuchs: "Theory of Dynamical Properties of Dielectric Surfaces"
S. A. Rice, D. Guidotti, H. L. Lemberg, W. C. Murphy, and A. N. Bloch: "Some Comments on the Electronic Properties of Liquid Metal Surfaces"

11. Title: Surface Properties of Materials
Edited by: L. L. Levenson Published: Surface Science 48, No. 1 (March 1975) 287 pages
Contains: Proceedings of the Conference on Surface Properties of Materials, University of Missouri, Rolla, Missouri, June 24-27, 1974. Contains sixteen articles on surface properties and surface characterization.
P. Auger: "The Auger Effect"
C. C. Chang: "General Formalism for Quantitative Auger Analysis"
J. P. Rynd and A. K. Rastogi: "Characterization of Glass Surfaces by Electron Spectroscopy"
J. E. Rowe, H. Ibach, and H. Froitzheim: "Photoemission and Energy Loss Spectroscopy on Semiconductor Surfaces"
D. L. Mills: "The Scattering of Low Energy Electrons by Electric Field Fluctuations near Crystal Surfaces"
R. L. Park: "Recent Developments in Appearance Potential Spectroscopy"
C. R. Brundle: "Elucidation of Surface Structure and Bonding by Photoelectron Spectroscopy?"
J. E. Holliday: "Characterization of Surfaces by Soft X-ray Spectroscopy"
A. V. Crewe: "Electron Microscopes using Field Emission Source"
G. Slodzian: "Some Problems Encountered in Secondary Ion Emission Applied to Elementary Analysis"
H. B. Huntington, L. A. Turk, and W. W. White III: "Binding of an Adatom to a Simple Metal Surface"
S. L. Bernasek and G. A. Somorjai: "Small Molecule Reactions on Stepped Single Crystal Platinum Surfaces"
R. C. O'Handley and D. K. Burge: "Optical Studies of Chemisorption on Metals"
P. Halevi: "Absorption of Radiation by Impurities on Crystalline Surfaces"
B. B. Dasgupta, P. Kumar, and D. E. Beck: "A Simple Dispersion Relation for the Surface Plasmon: Dependence on Electron Density Profile"
R. J. Bell, R. W. Alexander, Jr., C. A. Ward, and I. L. Tyler: "Introductory Theory for Surface Electromagnetic Wave Spectroscopy"

12. Title: Treatise on Solid State Chemistry. Vol. 6. Surfaces
Edited by: N. B. Hannay
Published: Plenum Press, New York, 1976
Contains: Ten articles on surface science
G. A. Somorjai: "The Structure and Thermodynamics of Clean Surfaces - Principles"
E. G. McRae and H. D. Hagstrum: "Surface Structure - Experimental Methods"
G. M. Rosenblatt: "Evaporation from Solids"
R.J.H. Voorhoeve: "Molecular Beam Deposition of Solids on Surfaces: Ultrathin Films"
T. N. Rhodin and D. L. Adams: "Adsorption of Gases on Solids"
T. E. Madey, J. T. Yates, Jr., D. R. Sandstrom, and R.J.H. Voorhoeve: "Catalysis by Solid Surfaces"
F. H. Eisen and J. W. Mayer: "Ion Implantation and Channeling"
S. R. Morrison: "Semiconductor Surfaces"
W. Vielstich et al.: "The Role of the Solid in Electrochemical Phenomena"
H. L. Frisch, G. L. Gaines, Jr., and H. Schonhorn: "Polymer Surfaces"

13. Title: Methods of Surface Analysis
Edited by: A. W. Czanderna
Published: Elsevier, New York, 1975
Contains: Ten articles on surface analysis
G. K. Wehner: "The Aspects of Sputtering in Surface Analysis Methods"
D. Lichtman: "A Comparison of the Methods of Surface Analysis and Their Applications"
T. M. Buck: "Low-Energy Ion Scattering Spectrometry"
W. M. Riggs and M. J. Parker: "Surface Analysis by X-ray Photoelectron Spectroscopy"
A. Joshi, L. E. Davis, and P. W. Palmberg: "Auger Electron Spectroscopy"
J. A. McHugh: "Secondary Ion Mass Spectrometry"
J. M. Morabito and R. K. Lewis: "The Use of Auger Electron Spectroscopy and Secondary Ion Mass Spectrometry in the Microelectronic Technology"
E. W. Müller: "The Atom-Probe Field Ion Microscope"
J. H. Block and A. W. Czanderna: "Field Ion Mass Spectrometry Applied to Surface Investigations"
H. G. Tompkins: "Infrared Reflection - Absorption Spectroscopy"

14. Title: Surface Physics of Phosphors and Semiconductors
Edited by: C. G. Scott and C. E. Reed
Published: Academic Press, New York, 1975
Contains: Nine articles on characterization and properties of semiconductor surfaces
D. Haneman: "Atomic Structures of Surfaces"
R. O. Jones: "Aspects of Surface State Theory"
F. Berz: "The Surface Space Charge Layer"
S. R. Morrison: "Theory of Adsorption"
C. E. Reed and C. G. Scott: "Techniques and Measurements"
F. Meyer and M. J. Sparnaay: "The Chemical and Physical Properties of Clean Germanium and Silicon Surfaces"
C. G. Scott and C. E. Reed: "II-VI and III-V Compound Materials"
J. N. Zemel: "Gas Effects on IV-VI Semiconductor Films"
K. H. Zaininger: "The Effect of Surface States on Semiconductor Devices"

15. Title: The Physical Basis for Heterogeneous Catalysis
Edited by: E. Drauglis and R. I. Jaffe
Published: Plenum Press, New York, 1976
Contains: 26 articles on the physical and chemical characterization of surfaces and on the use of modern surface science to study catalysts and catalytic reactions

16. Title: Interactions on Metal Surfaces. Vol. 4 of Topics in Applied Physics
Edited by: R. Gomer
Published: Springer-Verlag, New York, 1975
Contains: Seven articles on the characterization of surfaces and the study of catalytic reactions
J. R. Smith: "Theory of Electronic Properties of Surfaces"
S. K. Lyo and R. Gomer: "Theory of Chemisorption"
L. D. Schmidt: "Chemisorption - Aspects of the Experimental Situation"
D. Menzel: "Desorption Phenomena"
E. W. Plummer: "Photoemission and Field Emission Spectroscopy"
E. Bauer: "Low Energy Electron Diffraction (LEED) and Auger Methods"
M. Boudart: "Concepts in Heterogeneous Catalysis"

17. Title: Surfaces and Interfaces of Glass and Ceramics
Edited by: V. D. Frechette, W. C. LaCourse and V. L. Burdick
Published: Academic Press, New York, 1974
Contains: 26 articles on the characterization and properties of glass and ceramic surfaces.

18. Title: ARPA/NBS Workshop IV. Surface Analysis for Silicon Devices
Edited by: A. G. Lieberman
Published: National Bureau of Standards Special Publication 400-23 (March 1976)
Contains: 22 articles on various methods for the analysis and characterization of silicon and semiconductor surfaces

19. Title: Secondary Ion Mass Spectrometry
Edited by: K.F.J. Heinrich and D. E. Newbury
Published: National Bureau of Standards Special Publication 427 (October 1975)
Contains: Ten articles on the practice of secondary-ion mass spectroscopy
H. Liebl: "The Ion Microprobe - Instrumentation and Techniques"
G. Slodzian: "Looking at the Collection Efficiency Problem through the Ion Microscope Optics"
P. Williams and C. A. Evans, Jr.: "High Mass Resolution Secondary Ion Mass Spectrometry"
J. G. Bradley, D. Y. Jerome, and C. A. Evans, Jr.; "A Comparison of Mass Spectra from Three Ion Probes"
C. A. Andersen: "A Critical Discussion of the Local Thermal Equilibrium Model for the Quantitative Correction of Sputtered Ion Intensities"
J. M. Schroeer: "An Outline of Secondary Ion Emission Models"
J. A. McHugh: "Empirical Quantitation Procedures in SIMS"
J. F. Lovering: "Application of SIMS Microanalysis Techniques to Trace Element and Isotopic Studies in Geochemistry and Cosmochemistry"
J. A. McHugh: "Factors that Influence an Elemental Depth Concentration Profile"
J. M. Morabito: "A Comparison of Auger Electron Spectroscopy (AES) and Secondary Ion Mass Spectrometry (SIMS)"

20. Title: Proceedings of the 22nd National Symposium of the American Vacuum Society
Published: Journal of Vacuum Science and Technology 13, No. 1, January/February 1976
Contains: Proceedings of the National Symposium held at Philadelphia, Pennsylvania, on October 28-31, 1975. Contains many invited and contributed papers on a variety of topics pertaining to surface science, thin-film phenomena, and vacuum science and technology; electrical and chemical properties of interfaces; structural and mechanical properties of interfaces; properties of films and interfaces; thin films in tribology and mechanical properties of thin films; optical properties of thin films; applications of thin films; thin film processes; structure of surfaces; structure and analysis of surfaces; surface properties of III-V surfaces; chemistry at surfaces; chemisorption; catalysis; interactions of atoms with surfaces; ion-material interactions and techniques; profile analysis by various methods)

21. Title: Proceedings of the Third Annual Conference on the Physics of Compound Semiconductor Interfaces
Published: J. Vac. Sci. Technol. 13, No. 4, 749-964 (July/August 1976)
Contains: 37 articles on the characterization and properties of compound semiconductor surfaces and interfaces

22. Title: Systematic Materials Analysis (Vols. 1, 2, and 3)
Edited by: J. H. Richardson and R. V. Peterson
Published: Academic Press, New York, 1974
Contains: The following chapters pertaining to surface analysis:
G. Stupian: "Auger Electron Spectrometry" (Vol. 1)
H. H. Farrell: "Electron Diffraction: Low Energy (LEED)" (Vol. 1)
A. L. Smith: "Infrared Spectrometry" (Vol. 1)
J. J. Uebbing: "Ultraviolet Photoelectron Spectrometry" (Vol. 2)
W. G. Proctor: "X-ray Photoelectron Spectrometry (ESCA)" (Vol. 2)
R. S. Carbonara: "Ion-Scattering Spectrometry for Surface Analysis" (Vol. 3)

23. Title: Electronic Structure and Reactivity of Metal Surfaces
Edited by: E. G. Derovane and A. A. Lucas
Published: Plenum Press, New York, 1976
Contains: 17 articles on the theory, chemistry, reactivity, activity of metal surfaces
T. Rhodin and D. Adams: "Introduction to Phenomenological Models and Atomistic Concepts of Clean and Chemisorbed Surfaces"
T. A. Grimley: "Survey of Current Ideas in the Theory of Chemisorption by Metals"
G. Allan: "Electronic Structure of Transition Metal Surfaces"
N. D. Lang: "Density-Functional Approach to the Electronic Structure of Metal Surfaces and Metal-Adatom Systems
T. B. Grimley: "Chemisorption Theory, Electronic Structure, and Reactivity of Metal Surfaces"
T. Rhodin and D. Adams: "Electronic Properties of Clean and Chemisorbed Metal Surfaces"
T. Rhodin and D. Adams: "Approach to Two Prototype Metal Adsorption Systems"
G. E. Rhead: "Atomic Structure and Thermodynamics of Pure and Two-Component Metal Surfaces"
B. W. Holland: "Theory of L.E.E.D."
S. Andersson: "Applications of LEED to the Determination of Surface Structures on Metals"
J. W. Gadzuk: "Electron Spectroscopy of Surfaces via Field and Photoemission"
C. R. Brundle: "Electron Spectroscopy for the Investigation of Metallic Surfaces and Adsorbed Species"
M. Barber: "S.I.M.S. Studies at Metal Surfaces"
J. Block: "Field-Ion-Mass Spectrometry Investigating Electronic Structure and Reactivity of Surfaces"
C. Naccache: "Spectroscopic Studies of Supported Metal Catalysts: Electron and Ferromagnetic Resonance and Infrared Spectroscopy"
G. C. Bond: "Small Metal Particles: A Bridge between Theory and Practice"
V. Ponec: "Catalysis by Supported and Unsupported Metals and Alloys"

24. Title: Adsorption at Solid Surfaces
Published: Surface Science 53 (December 1975)
Contains: Proceedings of the Second Interdisciplinary Surface Science Conference, University of Warwick, March 17-20, 1975

25. Title: Surface Science: Recent Progress and Perspectives
Edited by: R. Vanselow and S. Y. Tong
Published: CRC Critical Reviews in Solid State Sciences 6, Nos. 2, 3, and 4 (1976)
Contains: Proceedings of the International Summer Institute in Surface Science, University of Wisconsin, Milwaukee, Wisconsin, August 1975. Contains 19 articles on recent developments of surface science.

E. W. Müller: "The Imaging Process in Field Ion Microscopy from the FEM to the Atom-Probe"
P. Soven, E. W. Plummer, and N. Kar: "Field Emission Energy Distribution (Clean Surfaces)"
J. H. Block: "Chemical Surface Reactions in the Presence of High Electric Fields"
B. Mutaftschiev: "Adsorption and Crystal Growth"
H. P. Bonzel: "Surface Diffusion of Metals: A Comparison of Intrinsic and Mass Transfer Measurements"
L. Esaki and L. L. Chang: "Superfine Structures of Semiconductors grown by Molecular Beam Epitaxy"
J. G. Dash: "Recent Studies of Physisorbed Films"
W. A. Steele: "Monolayer Physical Adsorption on Crystal Surfaces"
T. B. Grimley: "Chemisorption Theory"
M. B. Webb and P. I. Cohen: "Structural Studies of Clean and Overlayed Surfaces with an Application to Xe Adsorption on Ag"
R. L. Park and M. den Boer: "Surface Analysis using Electron Beams"
A. Benninghoven: "Surface Analysis by Means of Ion Beams"
W. E. Spicer: "Surface Analysis by Means of Photoemission and other Photon-stimulated Processes"
J. H. Lunsford: "Surface Analysis by Means of Magnetic Resonance Techniques"
J. A. Appelbaum and D. R. Hamann: "Quantum Physics and Chemistry of Surfaces"
T. Baker: "Controlled Atmosphere Electron Microscopy of Gas-solid Interactions"
T. E. Fischer: "Contributions of Surface Physics to Catalysis"
J. R. Arthur: "Surface Science in the Electronics Industry"
M. Kaminsky: "Surface Effects in Controlled Thermonuclear Fusion"

APPENDIX C. SUMMARY OF MEASUREMENT TECHNIQUES THAT HAVE BEEN USED TO CHARACTERIZE SURFACES.

Figure C.1 shows a summary of the many techniques that have been used to characterize surfaces; this summary has been adapted from one prepared recently by Murday [4]. The key to the various acronyms is given in table C.1.

TABLE C.1. KEY TO ACRONYMS SHOWN IN FIGURE C.1.

AEAPS - Auger-electron appearance-potential spectroscopy
AEM - Auger-electron microscopy
AES - Auger-electron spectroscopy
APS - Appearance-potential spectroscopy
ASW - Acoustic surface-wave measurements
ATR - Attenuated total reflectance
BIS - Bremsstrahlung isochromat spectroscopy
CIS - Characteristic isochromat spectroscopy
CL - Cathodoluminescence
COL - Colorimetry: ir, visible, uv, x-ray, and γ-ray absorption spectroscopy
CPD - Contact potential difference (work-function measurements)
DAPS - Disappearance-potential spectroscopy
ΔH_{ADS} - Heat of adsorption measurements
EL - Electroluminescence
ELL - Ellipsometry
EELS - Electron energy-loss spectroscopy
EM - Electron microprobe
ES - Emission spectroscopy
ESDI - Electron-stimulated desorption of ions
ESDN - Electron-stimulated desorption of neutrals
ESR - Electron-spin resonance
EXAFS - Extended x-ray absorption fine structure
FD - Flash desorption
FDM - Field-desorption microscopy
FDS - Field-desorption spectroscopy
FEM - Field-emission microscopy
FEES - Field-electron energy spectroscopy
FIM - Field-ion microscopy
FIM-APS - Field-ion microscope - atom probe spectroscopy
FIS - Field-ion spectroscopy
GDMS - Glow-discharge mass spectroscopy
GDOS - Glow-discharge optical spectroscopy
HEED - High-energy electron diffraction
IIRS - Ion-impact radiation spectroscopy
IIXS - Ion-induced x-ray spectroscopy
IMMA - Ion microprobe mass analysis
IMXA - Ion microprobe x-ray analysis
INS - Ion-neutralization spectroscopy
IRS - Internal reflectance spectroscopy
IS - Ionization spectroscopy
ISD - Ion-stimulated desorption
ISS - Ion-scattering spectroscopy
ITS - Inelastic tunneling spectroscopy
LEED - Low-energy electron diffraction
LMP - Laser microprobe
LS - Light scattering
MBRS - Molecular-beam reactive scattering
MBSS - Molecular-beam surface scattering
MOSS - Mossbauer spectroscopy
MS - Magnetic saturation
NIRS - Neutral impact radiation spectroscopy
NMR - Nuclear magnetic resonance
PD - Photodesorption
PEM - Photoelectron microscopy
PES - Photoelectron spectroscopy
RBS - Rutherford backscattering spectroscopy
RHEED - Reflection high-energy electron diffraction
SC - Surface capacitance
SDMM - Scanning desorption molecule microscopy
SEE - Secondary-electron emission
SEM - Scanning electron microscopy
SI - Surface ionization
$\sigma(p)$ - Adsorption isotherm measurements
SIIMS - Secondary-ion imaging mass spectroscopy
SIMS - Secondary-ion mass spectroscopy
SLEEP - Scanning low-energy electron probe
SRS - Surface reflectance spectroscopy
STEM - Scanning transmission electron microscopy
SXAPS - Soft x-ray appearance - potential spectroscopy
SXES - Soft x-ray emission spectroscopy
TE - Thermionic emission
TEM - Transmission electron microscopy
TL - Thermoluminescence
UPS - Ultraviolet photoemission spectroscopy
XEM - Exoelectron microscopy
XES - Exoelectron spectroscopy
XPS - X-ray photoemission spectroscopy
XRD - X-ray diffraction (glancing incidence)

INCIDENT PROBE	DETECTED PARTICLE: PHOTON	ELECTRON	NEUTRAL	ION	PHONON	E/H FIELD
PHOTON	ATR ELL ESR EXAFS IRS LS MOSS NMR SRS XRD	AEAPS AEM AES PEM PES SEE UPS XEM XES XPS	LMP PD	LMP PD		
ELECTRON	APS BIS CL CIS EM SXAPS SXES	AEAPS AEM AES DAPS EELS HEED IS LEED SEE RHEED SEM SLEEP STEM TEM	ESDN SDMM	ESDI		
NEUTRAL	NIRS	SEE	MBRS MBSS $\sigma(p)$		ΔH_{ADS}	
ION	GDOS IIRS IIXS	IMXA INS SEE	ISD SDMM	GDMS IMMA ISD ISS RBS SIIMS SIMS		
PHONON	ES TL	TE	FD	SI	ASW	
E/H FIELD	EL	FEES FEM ITS	FDM FDS	FIM FIM-APS FIS		CPD MS SC

Figure C.1. Outline of surface-characterization techniques.

APPENDIX D. LIST OF RECENT PUBLICATIONS ON SURFACE-RELATED MEASUREMENTS BY STAFF OF THE INSTITUTE FOR BASIC STANDARDS

This appendix lists publications dealing with surface-related measurements by the NBS staff who have been involved with the programs described in sections 4.1 and 4.2.

1. Condensation of Tungsten on Tungsten in Atomic Detail: Monte Carlo and Statistical Calculations vs. Experiment, R. D. Young and D. C. Schubert, J. Chem. Phys. 42, 3943 (1965).
2. Condensation of Tungsten on Tungsten in Atomic Detail: Observation with the Field-Ion Microscope, T. Gurney, F. Hutchinson, and R. D. Young, J. Chem. Phys. 42, 3939 (1965).
3. Field Desorption of Thorium from a Field-Evaporated Tungsten Surface, R. D. Young, J. Appl. Phys. 36, 2656 (1965).
4. Differences in the Characteristic Electron Energy Loss Spectra of Solid and Liquid Bismuth, C. J. Powell, Phys. Rev. Lett. 15, 852 (1965).
5. Field Emission Ultramicrometer, R. D. Young, Rev. Sci. Instrum. 37, 275 (1966).
6. Inelastic Scattering Cross Sections for 20 keV Electrons in Al, Be and Polystyrene, N. Swanson and C. J. Powell, Phys. Rev. 145, 195 (1966).
7. Plasmon Damping Metals, B. W. Ninham, C. J. Powell, and N. Swanson, Phys. Rev. 145, 209 (1966).
8. Effect of Surface Patch Fields on Field-Emission Work-Function Determinations, R. D. Young and H. E. Clark, Phys. Rev. Lett. 17, 351 (1966).
9. Anomalous Energy Spreads in Electron Beams, J. A. Simpson and C. E. Kuyatt, J. Appl. Phys. 37, 3805 (1966).
10. Anomalous Work Function of the Tungsten (110) Plane, R. D. Young and H. E. Clark, Appl. Phys. Lett. 9, 265 (1966).
11. Electron Monochromator Design, C. E. Kuyatt and J. A. Simpson, Rev. Sci. Instrum. 38, 103 (1967).
12. Characteristic Energy Losses of 8 keV Electrons in Liquid In-Al and In-Bi Alloys, C. J. Powell, Adv. Phys. 16, 203 (1967).
13. Inelastic Scattering of Kilovolt Electrons by Solids and Liquids: Determination of Energy Losses, Cross Sections, and Correlations with Optical Data, C. J. Powell, Health Phys. 13, 1265 (1967).
14. Field Emission Ultramicrometer Checks Dimensions, Profiles without Contact, R. D. Young, Machinery Magazine (1967).
15. 1.1.5. Electron Guns, J. A. Simpson, *Methods of Experimental Phys. Vol. 4, Atomic and Electron Physics,* Academic Press, New York (1967).
16. 1.1.7. Special Sources of Monoenergetic Electrons, J. A. Simpson, *Methods of Experimental Phys., Vol. 4, Atomic and Electron Physics,* Academic Press, New York (1967).
17. Comparison of the Spherical Deflector and the Cylindrical Mirror Analyzers, H. Hafner, J. A. Simpson, and C. E. Kuyatt, Rev. Sci. Instrum. 39, 33 (1968).
18. Characteristic Energy-Loss Spectra and $-\mathrm{Im}(1/\varepsilon)$ for Amorphous and Polycrystalline Al_2O_3, N. Swanson, Phys. Rev. 165, 1067 (1968).
19. Excitation of L-Shell Electrons in Al and Al_2O_3 by 20 keV Electrons, N. Swanson and C. J. Powell, Phys. Rev. 167, 592 (1968).
20. Excitation of K-Shell Electrons in Be by Soft X-rays and 20 keV Electrons, N. Swanson and K. Codling, J. Opt. Soc. Am. 58, 1192 (1968).
21. 9.2. Interaction of Electrons with Solids, C. J. Powell, *Methods of Experimental Phys. Vol. 7, Part B, Atomic and Electron Physics,* p. 275, Academic Press, New York (1968).
22. Resolution Determination in Field Emission Energy Analyzers, R. D. Young and C. E. Kuyatt, Rev. Sci. Instrum. 39, 1477 (1968).
23. Characteristic Energy Losses of 8 keV Electrons in Liquid Al, Bi, In, Ga, Hg, and Au, C. J. Powell, Phys. Rev. 175, 972 (1968).
24. Field Emission through Single Strontium Atoms Adsorbed on a Tungsten Surface, H. E. Clark and R. D. Young, Surf. Sci. 12, 385 (1968).
25. Resonance Tunneling of Field Emitted Electrons through Adsorbates on Metal Surfaces, E. W. Plummer, J. W. Gadzuk, and R. D. Young, Solid State Commun. 7, 487 (1969).
26. Analysis of Optical- and Inelastic-Electron-Scattering Data. Parametric Calculations, C. J. Powell, J. Opt. Soc. Am. 59, 738 (1969).
27. Many-Body Tunneling-Theory Approach to Field Emission of Electrons from Solids, J. W. Gadzuk, Surf. Sci. 15, 466 (1969).

28. Band-Structure Effects in the Field-Induced Tunneling of Electrons from Metals, J. W. Gadzuk, Phys. Rev. 182, 416 (1969).
29. Resonance Tunneling Through Impurity States in Metal-Insulator-Metal Junctions, J. W. Gadzuk, J. Appl. Phys. 41, 286 (1970).
30. Analysis of Optical- and Inelastic-Electron-Scattering Data. II. Application to Al, C. J. Powell, J. Opt. Soc. Am. 60, 78 (1970).
31. Analysis of Optical- and Inelastic-Electron-Scattering Data. III. Reflectance Data for Beryllium, Germanium, Antimony, and Bismuth, C. J. Powell, J. Opt. Soc. Am. 60, 214 (1970).
32. Resonance Transmission in Electron Emission from Surfaces with Adsorbed Atoms, J. W. Gadzuk, Surf. Sci. 18, 193 (1969).
33. Coupled Surface-Plasmon Modes in Metal-Thin-Film-Vacuum Sandwiches, J. W. Gadzuk, Phys. Rev. B. 1, 1267 (1970).
34. Resonance-Tunneling Spectroscopy of Atoms Adsorbed on Metal Surfaces: Theory, J. W. Gadzuk, Phys. Rev. B 1, 2110 (1970).
35. Field-Emission Studies of Electronic Energy Levels of Adsorbed Atoms, E. W. Plummer and R. D. Young, Phys. Rev. B 1, 2088 (1970).
36. A Comparison Between the Fermi-Thomas and Quantum Dielectric Response of a Metal Surface to a Static Point Charge, J. W. Gadzuk, Surf. Sci. 23, 58 (1970).
37. Validity of Inelastic-Electron-Scattering Data in Determining the Metallic or Insulating Properties of Adsorbed Atomic Layers, C. J. Powell, Phys. Rev. B 1, 4191 (1970).
38. Comparison of Optical Data for Sodium and Potassium with Interband-Transition Absorption Theory, C. J. Powell, Optics Commun. 2, 87 (1970).
39. Surface States on Tungsten, E. W. Plummer and J. W. Gadzuk, Phys. Rev. Lett. 25, 1493 (1970).
40. Hot-Hole-Electron Cascades in Field Emission from Metals, J. W. Gadzuk and E. W. Plummer, Phys. Rev. Lett. 26, 92 (1971).
41. Field Emission Energy Distributions of Hydrogen and Deuterium on the (100) and (110) Planes of Tungsten, E. W. Plummer and A. E. Bell, J. Vac. Sci. Technol. 9 (1971).
42. Reply to Comments on a Theory of Field-Induced Tunneling, J. W. Gadzuk, Phys. Rev. B 3, 1772 (1971).
43. Virtual Impurity Level Density of States as Investigated by Resonance Tunneling, J. W. Gadzuk, E. W. Plummer, H. E. Clark, and R. D. Young, NBS Spec. Publ. 323 (1971).
44. Tunneling from Cambridge Surface States, J. W. Gadzuk, J. Vac. Sci. Technol. 9, 591 (1971).
45. Approach to Alkali-Metal Chemisorption within the Anderson Model, J. W. Gadzuk, J. K. Hartman, and T. N. Rhodin, Phys. Rev. B 4, 241 (1971).
46. Internal X-Ray Photoemission in Aluminum: Excitation of Electrons from the Valence Band, C. J. Powell, Solid State Commun. 10, 1161 (1972).
47. High-Resolution Measurements of Auger-Electron and Photoelectron Structure in the Secondary-Electron Energy Distributions of Aluminum, Nickel and Copper, C. J. Powell, Proc. International Conference on Inner Shell Ionization Phenomena and Future Applications, Atlanta, Ga. (1972).
48. Electron Spectroscopy of Chemisorbed Atoms, J. W. Gadzuk, IX Winter School of Theoretical Physics in Karpacz, Poland (1972) (*The Theory of Metals and the Many Body Problem, Vol. 11*, 1 (1972)).
49. Structure on the High-Energy Side of the $KL_{23}M$ Auger Peak from Solid Aluminum: Internal Photoemission, C. J. Powell, Appl. Phys. Lett. 20 (1972).
50. Photoemission Observation of a Surface State of Tungsten, B. J. Waclawski and E. W. Plummer, Phys. Rev. Lett. 29, 783 (1972).
51. High-Resolution Measurements of the $L_3M_{2,3}M_{4,5}$ Transitions in Nickel and Copper, C. J. Powell and A. Mandl, Phys. Rev. Lett. 29, 1153 (1972).
52. High-Resolution Measurements of Auger-Electron and Photoelectron Structure in the Secondary-Electron Energy Distributions of Aluminum, Nickel and Copper, C. J. Powell and A. Mandl, Phys. Rev. B 6, 4418 (1972).
53. Windowless Photoelectron Spectrometer for High Resolution Studies of Solids and Surfaces, J. K. Cashion, J. L. Mees, D. E. Eastman, J. A. Simpson, and C. E. Kuyatt, Rev. Sci. Instrum. 42, no. 11, 1670 (1971).
54. Third-Order Aberration Coefficients of Electron Lenses, C. E. Kuyatt, S. V. Natali, and D. DiChio, Proceedings Eleventh Symposium on Electron, Ion, and Laser Beam Technology, University of Colorado, Boulder, San Francisco Press, Inc. (1971).

55. Accurate Calculations of Properties of the Two-Tube Electrostatic Lens. I. Improved Digital Methods for the Precise Calculation of Electric Fields and Trajectories, S. Natali, D. DiChio, and C. E. Kuyatt, J. Res. Natl. Bur. Stand. 76A, 27 (1972).
56. Accurate Calculation of Properties of the Two-Tube Electrostatic Lens. II. First-Order Focal Properties and P-Q Curves, S. Natali, D. DiChio, E. Uva, and C. E. Kuyatt, Rev. Sci. Instrum. 43, 80 (1972).
57. Accurate Calculation of Properties of the Two-Tube Electrostatic Lens. III. Aberration Coefficients, C. E. Kuyatt, S. Natali, and D. DiChio, Rev. Sci. Instrum. 43, 84 (1972).
58. Field Emission Deflection Energy Analyzer, C. E. Kuyatt and E. W. Plummer, Rev. Sci. Instrum. 43, 108 (1972).
59. Contrasting Valence-Band Auger-Electron Spectra for Silver and Aluminum, C. J. Powell, Phys. Rev. Lett. 30, 1179 (1973).
60. Field-Emission Tails and Tunneling Lifetimes, J. W. Gadzuk and A. A. Lucas, Phys. Rev. B 7, 4770 (1973).
61. Field Emission Energy Distribution (FEED), J. W. Gadzuk and E. W. Plummer, Rev. Mod. Phys. 45, 487 (1973).
62. Semiautomated Data-Recording and Control System for an Electron Energy Analyzer, C. J. Powell, Rev. Sci. Instrum. 44, 1031 (1973).
63. Electronic Characterization of Submonolayer Films, E. W. Plummer, *Monolayer and Submonolayer Helium Films,* Symposium at Stevens Institute of Technology (1973).
64. Representation of Focal Properties of the Equal-Diameter Two-Tube Electrostatic Lens for Computer Calculations, A. Galejs and C. E. Kuyatt, J. Vac. Sci. Technol. 10, 1114 (1973).
65. Focal Properties of the Two-Tube Electrostatic Lens for Large Voltage Ratios, C. E. Kuyatt, D. DiChio, and S. V. Natali, J. Vac. Sci. Technol. 10, 1118 (1973).
66. Third-Order Aberration Coefficients of Electron Lenses. II, C. E. Kuyatt, D. DiChio, and S. V. Natali, J. Vac. Sci. Technol. 10, 1124 (1973).
67. Electron Energy Analyzer Design, C. E. Kuyatt, Proceedings of Conference on Electron Probe Analysis and Electron Microscopy, New Orleans, La. (1973).
68. Field Emission as a Probe of the Surface Density of States, D. R. Penn and E. W. Plummer, Phys. Rev. B 9, 1216 (1974).
69. Valence-Band Auger-Electron Spectra for Aluminum, J. W. Gadzuk, Phys. Rev. B 9, 1978 (1974).
70. Surface Molecules and Chemisorption. I. Adatom Density of States, J. W. Gadzuk, Surf. Sci. 43, 44 (1974).
71. Use of Matrices to Represent Electron Lenses. Matrices for the Two-Tube Electrostatic Lens, D. DiChio, S. V. Natali, C. E. Kuyatt, and A. Galejs, Rev. Sci. Instrum. 45, 566 (1974).
72. Focal Properties of the Two-Tube Electrostatic Lens for Large and Near-Unity Voltage Ratios, D. DiChio, S. V. Natali, and C. E. Kuyatt, Rev. Sci. Instrum. 45, 559 (1974).
73. Attenuation Lengths of Low-Energy Electrons in Solids, C. J. Powell, Surf. Sci. 44, 29 (1974).
74. Third-Order Asymptotic Aberration Coefficients of Electron Lenses. III. Formulas and Results for the Two-Tube Electrostatic Lens, C. E. Kuyatt, D. DiChio, and S. V. Natali, Rev. Sci. Instrum. 45, 1275 (1974).
75. Angular Distributions of Electrons Photoemitted from Chemisorbed Atoms, J. W. Gadzuk, Solid State Commun. 15, 1011 (1974).
76. Photoelectron Spectra of the Decomposition of Ethylene on (110) Tungsten, E. W. Plummer, B. J. Waclawski, and T. V. Vorburger, Chem. Phys. Lett. 28, 510 (1974).
77. Surface Molecules and Chemisorption. II. Photoemission Angular Distributions, J. W. Gadzuk, Phys. Rev. B 10, 5030 (1974).
78. A New Form for the Third-Order Asymptotic Aberration Coefficients of Electrostatic Lenses; Application to the Two-Tube Electrostatic Lens, D. DiChio, S. V. Natali, and C. E. Kuyatt, Rev. Sci. Instrum. 46, 71 (1975).
79. Determination of Electron Attenuation Lengths in Metals: Transmission through Thin Adsorbed Films, M. Sunjić, D. Sokcović, and J. W. Gadzuk, J. Appl. Phys. Jap. Suppl. 2, Pt. 2, 753 (1974) (Proceedings Second Internatl. Conf. on Solid Surfaces).
80. Electron Spectroscopy of Chemisorbed Atoms and Surface Molecules, J. W. Gadzuk, J. Appl. Phys. Jap. Suppl. 2, Pt. 2, 851 (1974) (Proceedings Second Internatl. Conf. on Solid Surfaces).
81. Experimental Observations of Electronic Energy Levels at a Solid-Vacuum Interface, E. W. Plummer, B. J. Waclawski, and T. Vorburger, Proceedings of the Symposium on Electrocatalysis, San Francisco, 43 (1974).

82. Relaxation Energies in Chemisorption Spectroscopy, J. W. Gadzuk, J. Vac. Sci. Technol. 12, 289 (1975).
83. Angular Dependence of UV Photoelectron Distributions for Oxygen Adsorbed on W(100), B. J. Waclawski, T. V. Vorburger, and R. J. Stein, J. Vac. Sci. Technol. 12, 301 (1975).
84. Determination of the Spin-Polarized Surface Density of States in Strongly Correlated Metals by Field Emission: Theory, D. R. Penn, Phys. Rev. B 11, 3208 (1975).
85. Vacuum-Tunneling Spectroscopy, E. W. Plummer, J. W. Gadzuk, and D. R. Penn, Physics Today 28 (1975).
86. Field Emission Work Functions, T. V. Vorburger, D. Penn, and E. W. Plummer, Surf. Sci. 48, 417 (1975).
87. Optical Properties of Adsorbate Atoms, A. J. Bennett and D. R. Penn, Phys. Rev. B 11, 3644 (1975).
88. Field-Ion Microscopy of Silicon, A. J. Melmed and R. J. Stein, Surf. Sci. 49, 645 (1975).
89. The Dependence of the Tunneling Current on Density of States in Non-Superconducting Junctions, D. R. Penn, Surf. Sci. 50, 125 (1975).
90. 5f-Electron Excitation Energies and the Coulomb Term, U, in the Light Actinide Metals, J. F. Herbst and R. E. Watson, Phys. Rev. Lett. 34, 1395 (1975).
91. Excitation Energy Dependence of Core-Level X-Ray-Photoemission-Spectra Line Shapes in Metals, J. W. Gadzuk and M. Šunjić, Phys. Rev. B 12, 524 (1975).
92. Measurement of the Surface Density of States by Field Ionization, D. R. Penn, Surf. Sci. 52, 270 (1975).
93. Observation of Polarized Electrons by Davisson and Germer, C. E. Kuyatt, Phys. Rev. B 12, 4581 (1975).
94. Interaction of Atoms and Molecules with Surfaces, J. W. Gadzuk, *Surface Physics of Materials*, Vol. II, 339 (1975).
95. Extra-Molecular Relaxation Energies for H_2 Embedded in an Electron Gas, J. W. Gadzuk, Chem. Phys. Lett. 36, 606 (1975).
96. Angle-Resolved Photoemission from Chemisorbed Layers: Further Theoretical Considerations, J. W. Gadzuk, Surf. Sci. 53, 132 (1975).
97. Angle-Resolved Photoemission from Crystal-Field Split d Shells of Adsorbed Atoms, J. W. Gadzuk, Phys. Rev. B 12, 5608 (1975).
98. Photoemission for Xe Physisorbed on W(100): Evidence for Surface Crystal-Field Effects, B. J. Waclawski and J. F. Herbst, Phys. Rev. Lett. 35, 1594 (1975).
99. Cross Sections for Ionization of Inner-Shell Electrons by Electrons, C. J. Powell, Rev. Mod. Phys. 48, 33 (1976).
100. Cross Sections for Ionization of Inner-Shell Electrons by Electron Impact, C. J. Powell, J. Vac. Sci. Technol. 13, 219 (1976).
101. Electron Attenuation Lengths for Free-Electron-Like Metals, D. R. Penn, J. Vac. Sci. Technol. 13, 221 (1976).
102. UPS Studies of Virgin CO on W(100), T. V. Vorburger, D. R. Sandstrom, and B. J. Waclawski, J. Vac. Sci. Technol. 13, 287 (1976).
103. Can Chemisorption Bonding Shifts be Separated from Relaxation-Energy Shifts in Photo-Electron Spectroscopy?, J. W. Gadzuk, J. Vac. Sci. Technol. 13, 343 (1976).
104. 4f Excitation Energies in Rare-Earth Metals: Relativistic Calculations, J. F. Herbst, R. E. Watson, and J. W. Wilkins, Phys. Rev. B 13, 1439 (1976).
105. Effect of Ground State and Excitation Potentials on Energy Levels of Ni Metal, R. E. Watson, J. F. Herbst, L. Hodges, B. I. Lundqvist, and J. W. Wilkins, Phys. Rev. B 13, 1463 (1976).
106. Improved Microwave-Discharge Source for UV Photoemission, T. V. Vorburger, B. J. Waclawski, and D. R. Sandstrom, Rev. Sci. Instrum. 47, 501 (1976).
107. Core Level Shifts in the 3d Transition Metals and Tin, R. E. Watson, M. L. Perlman, and J. F. Herbst, Phys. Rev. B 13, 2358 (1976).
108. Quantitative Chemical Analysis by ESCA, D. R. Penn, J. Electron Spectrosc. 9, 29 (1976).
109. Photoelectron Spectra of Adsorbed Species on Tungsten, E. W. Plummer, B. J. Waclawski, T. V. Vorburger, and C. E. Kuyatt, Prog. Surf. Sci. 7, 149 (1976).
110. Electron Spectroscopy of Surfaces via Field and Photoemission, J. W. Gadzuk, *Electronic Structure and Reactivity of Metal Surfaces*, Plenum Publishing Corp. (1976).
111. Comment on "Field Emission as a Probe of the Surface Density of States," D. R. Penn, Phys. Rev. B 14, 849 (1976).
112. Screening Energies in Photoelectron Spectroscopy of Localized Electron Levels, J. W. Gadzuk, Phys. Rev. B 14, 2267 (1976).
113. Coulomb Term U and 5f Electron Excitation Energies for the Metals Actinium to Berkelium, J. F. Herbst, R. E. Watson, and I. Lindgren, Phys. Rev. B 14, 3265 (1976).

114. Vibrational Excitation in Photoemission Spectroscopy of Condensed Molecules, J. W. Gadzuk, Phys. Rev. B 14, 5458 (1976).
115. Absolute Yields of Auger Electrons from Beryllium and Aluminum under Proton Bombardment: Determination of the Attenuation Lengths of Low-Energy Electrons in Solids, C. J. Powell, R. J. Stein, P. B. Needham, and T. J. Driscoll, Phys. Rev. B, to be published.
116. Angle Resolved Auger Surface Spectroscopy, J. W. Gadzuk, Surf. Sci., to be published.
117. Angle-Resolved Photoemission from Crystal-Field-Split Adatom Levels, J. F. Herbst, Phys. Rev. B, to be published.
118. Angle-Resolved Photoemission from Physisorbed Atoms, J. F. Herbst, Proceedings Photoemission from Surfaces Conference, Noordwijk, The Netherlands (1976), to be published.
119. Determination of the Be KVV-Auger-Electron Attenuation Length in Be using 160 keV Protons, P. B. Needham, T. J. Driscoll, C. J. Powell, and R. J. Stein, Appl. Phys. Lett., to be published.
120. Displacement of Hydrogen by Carbon Monoxide on the (100) Face of Tungsten: A Photoemission and Thermal Desorption Study, T. V. Vorburger, D. R. Sandstrom, and B. J. Waclawski, Surf. Sci., to be published.
121. Effective Crystal Fields in the Rare Earth Pnictides, J. F. Herbst, P. Bak, and R. K. Watson, Proceedings International Conference on Magnetism, Amsterdam, The Netherlands (1976).
122. Electron Mean Free Paths for Free-Electron-Like Materials, D. R. Penn, Phys. Rev. B, to be published.
123. Electron Transmission Measurements of Electron Mean Free Path in Supported Thin Films from 1-5 keV, R. J. Stein, Surf. Sci., to be published.
124. Emission of Polarized Electrons from Solids, M. Campagna, D. T. Pierce, F. Meier, K. Sattler, and H. C. Siegmann, *Adv. Electronics and Electron Physics,* L. Marton, ed., to be published.
125. Evaluation of Formulas for Inner-Shell Ionization Cross Sections, C. J. Powell, NBS Special Publication, to be published.
126. Evidence for the Distortion of C_2H_4 and C_2H_2 Chemisorbed on W(100), T. V. Vorburger, B. J. Waclawski, and E. W. Plummer, Chem. Phys. Lett., to be published.
127. Many Body Effects in Photoemission, J. W. Gadzuk, *Photoemission from Surfaces,* J. Wiley, publisher, B. Feuerbacher, B. Fitton, and R. Willis, editors, to be published.
128. Plasmon Satellites in X-ray Photoemission Spectra, J. W. Gadzuk, Phys. Rev. B, Comments and Addenda, to be published.
129. The Role of Electronic Structure in Catalysis, J. W. Gadzuk and R. E. Watson, NBS Spec. Publ., to be published.
130. Secondary Electron Energy Distribution in High Energy Photoemission, D. R. Penn, J. Vac. Sci. Technol., to be published.
131. Theory of the Electron Energy Loss Spectrum in Core Level X-ray Photoemission from Solids, D. R. Penn, Phys. Rev. Lett., to be published.
132. Time Scales and Plasmon Satellites in XPS, J. W. Gadzuk, Proceedings of Photoemission from Surfaces Conferences, Noordwijk, The Netherlands, to be published.

REFERENCES

[1] Physics in Perspective, Vol. II, Part A, p. 547 (National Academy of Sciences, Washington, D.C., 1972).

[2] Materials and Man's Needs, Materials Science and Engineering, p. 142 (National Academy of Sciences, Washington, D.C. (1974)).

[3] Duke, C. B., and Park, R. L., Surface structure - An emerging spectroscopy, Phys. Today 25, No. 8, 23-31 (Aug. 1972).

[4] Murday, J. S., Review of surface physics, Naval Research Laboratory Memorandum Report 3062 (May 1975).

[5] Park, R. L., Introduction to surface spectroscopies, Experimental Methods in Catalytic Research, Vol. 3, pp. 1-39, Ed. R. B. Anderson and P. T. Dawson (Academic Press, N. Y., 1976).

[6] Characterization of Solid Surfaces, Ed. P. F. Kane and G. R. Larrabee (Plenum Press, N. Y., 1974).

[7] (a) Coburn, J. W., and Kay, E., Techniques for elemental composition profiling in thin films, CRC Critical Reviews in Solid State Sciences 4, No. 4, 561-590 (1974);
(b) Coburn, J. W., Sputtering in the Surface Analysis of Solids: A Discussion of some Problems, J. Vac. Sci. Technol. 13, No. 5, 1037-1044 (Sept./Oct. 1976).

[8] Surface Science: Recent Progress and Perspectives (Proc. International Summer Institute in Surface Science, University of Wisconsin, Milwaukee, Aug. 27-31, 1973), Ed. T. S. Jayadevaiah and R. Vanselow, CRC Critical Reviews in Solid State Sciences 4, Nos. 2 and 3 (1974).

[9] Pendry, J. B., Low Energy Electron Diffraction (Academic Press, N. Y., 1974).

[10] Surface Physics of Materials, Ed. J. M. Blakely (Academic Press, N. Y., 1975).

[11] (a) Schrieffer, J. R., and Soven, P., Theory of the electronic structure, Phys. Today 28, No. 4, 24-30 (Apr. 1975);
(b) Estrup, P. J., The geometry of surface layers, Phys. Today 28, No. 4, 33-41 (Apr. 1975);
(c) Eastman, D. E., and Nathan, M. I., Photoelectron spectroscopy, Phys. Today 28, No. 4, 44-51 (Apr. 1975);
(d) Park, R. L., Inner-shell spectroscopy, Phys. Today 28, No. 4, 52-59 (Apr. 1975);
(e) Plummer, E. W., Gadzuk, J. W., and Penn, D. R., Vacuum-tunneling spectroscopy, Phys. Today 28, No. 4, 63-71 (Apr. 1975).
(f) Rhodin, T. N., and Tong, D.S.Y., Structure Analysis of Solid Surfaces, Phys. Today 28, No. 10, 23-32 (Oct. 1975).

[12] Brundle, C. R., The application of electron spectroscopy to surface studies, J. Vac. Sci. Technol. 11, No. 1, 212-224 (1974);

[13] Hagstrum, H. D., Electronic characterization of solid surfaces, Science 178, No. 4058, 275-282 (Oct. 20, 1972).

[14] Treatise on Solid State Chemistry, Surfaces, Vol. 6, Ed. N. B. Hannay (Plenum Press, N.Y., 1976).

[15] Surface Physics of Phosphors and Semiconductors, Ed. C. G. Scott and C. E. Reed (Academic Press, N.Y., 1975).

[16] (a) Evans, C. A., Jr., Surface and Thin Film Compositional Analysis: Description and comparison of techniques, Anal. Chem. 47, No. 9, 818A-829A (August 1975);
(b) Evans, C. A., Jr., Surface and Thin Film Analysis, Anal. Chem. 47, No. 9, 855A-866A (August 1975).

[17] Anderson, J. R., Structure of Metallic Catalysts (Academic Press, N.Y., 1975).

[18] Hagstrum, H. D., Rowe, J. E., and Tracy, J. C., Electron Spectroscopy of Solid Surfaces, Experimental Methods in Catalytic Research, Vol. 3, pp. 42-120, Ed. R. B. Anderson and P. T. Dawson (Academic Press, N.Y., 1976).

[19] Methods and Phenomena, Methods of Surface Analysis, Vol. 1, Ed. A. W. Czanderna (American Elsevier Publ. Co., N.Y., 1975).

[20] Prutton, M., Surface Physics (Oxford University Press, London, 1975).

[21] Oudar, J., Physics and Chemistry of Surfaces (Blackie, Glasgow, 1975).

[22] Ertl, E., and Küppers, J., Low-Energy Electrons and Surface Chemistry (Verlag Chemie, Weinheim, 1974).

[23] Honig, R. E., Surface and Thin Film Analysis of Semiconductor Materials, Thin Solid Films 31, Nos. 1 and 3, 89-122 (Jan. 1976).

[24] Fadley, C. S., Solid-State- and Surface-Analysis by means of Angular-Dependent X-ray Photoelectron Spectroscopy, Progress in Solid State Chemistry, Ed. G. Somorjai and J. McCaldin (Pergamon Press, N.Y., 1976).

[25] Taglauer, E., and Heiland, W., Surface Analysis with Low Energy Ion Scattering, Appl. Phys. 9, No. 4, 261-275 (1976).
[26] Niehus, H., and Bauer, E., Quantitative Aspects of Ion Scattering Spectroscopy (ISS), Surf. Sci. 47, No. 1, 222-233 (January 1975).
[27] Herglotz, H. K., and Suchan, H. L., ESCA - A New Tool for Surface Research, Advances in Colloid and Interface Science 5, 79-103 (1975).
[28] Swingle, R. S., and Riggs, W. M., ESCA, CRC Critical Reviews in Analytical Chemistry 5, No. 3, 267-321 (October 1975).
[29] Phillips, J. C., Semiconductor Surface Spectroscopy, J. Vac. Sci. Technol. 13, No. 1, 178-182 (Jan./Feb., 1976).
[30] Surface Measurement Technology: ARPA/NBS Workshop IV, Surface Analysis for Silicon Devices, Ed. A. G. Lieberman, NBS Special Publication SP400-23 (March 1976).
[31] The Physical Basis for Heterogeneous Catalysis, Ed. E. Drauglis and R. I. Jaffe (Plenum, N.Y., 1975).
[32] Surfaces and Interfaces of Glass and Ceramics, Ed. V. D. Fréchette, W. C. LaCourse, and V. L. Burdick (Plenum, N.Y., 1974).
[33] Interactions on Metal Surfaces, Vol. 4 of Topics in Applied Physics, Ed. R. Gomer (Springer-Verlag, Berlin, 1975).
[34] Systematic Materials Analysis, Ed. J. H. Richardson and R. V. Peterson (Academic Press, N.Y., 1974).
[35] Müller, E. W., and Tsong, T. T., Field Ion Microscopy, Principles and Applications (Elsevier, N. Y., 1969).
[36] Somorjai, G. A., Principles of Surface Chemistry (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1972).
[37] Aspects of the study of surfaces, Ed. I. Prigogine and S. A. Rice, Advances in Chemical Physics, Vol. 27 (John Wiley and Sons, N. Y., 1974).
[38] Ponec, V., Knor, Z., and Cerny, S., Adsorption on Solids (CRC Press, Cleveland, 1974).
[39] Baker, A. D., Brisk, M. A., and Liotta, D. C., Electron Spectroscopy: Ultraviolet Excitation, Anal. Chem. 48, No. 5, 281R-294R (April 1976).
[40] Hercules, D. M., Electron Spectroscopy: X-ray and Electron Excitation, Anal. Chem. 48, No. 5, 294R-313R (April 1976).
[41] Proc. International Summer Institute in Surface Science, University of Wisconsin, Milwaukee, August 18-22, 1975, Eds. R. Vanselow and S. Y. Tong, CRC Critical Reviews in Solid State Sciences Vol. 6, Nos. 2, 3, and 4 (1976).
[42] The Solid-Vacuum Interface, Proceedings of the Third Symposium on Surface Physics, University of Utrecht, The Netherlands, June 26-28, 1974, Surface Science 47, No. 1 (January 1975).
[43] Surface Properties of Materials, Proceedings of the Conference on Surface Properties of Materials, University of Missouri-Rolla, June 24-27, 1974, Surface Science 48, No. 1 (March 1975).
[44] Adsorption at Solid Surfaces, Proceedings of the Second Interdisciplinary Surface Science Conference, University of Warwick, England, March 17-20, 1975, Surface Science 53 (Dec. 1975).
[45] A General Discussion on Electron Spectroscopy of Solids and Surfaces, University of British Columbia, Vancouver, July 15-17, 1975, Faraday Discussions of the Chemical Society, No. 60 (1975).
[46] Electron Spectroscopy, Progress in Research and Applications, Proc. of the International Conference on Electron Spectroscopy, Namur, April 16-19, 1974, J. Electron Spectrosc. and Related Phenomena 5 (Nov./ Dec. 1974).
[47] Carlson, T. A., Photoelectron and Auger Spectroscopy (Plenum Press, N.Y., 1975).
[48] Proceedings of the Symposium on Electrocatalysis, The Electrochemical Society, San Francisco, May 13-15, 1974, Ed. M. W. Breiter (The Electrochemical Society, Princeton, 1974).
[49] Proceedings of the Third Annual Conference on the Physics of Compound Semiconductor Interfaces, San Diego, Calif., February 3-5, 1976, J. Vac. Sci. Technol. 13, No. 4, 749-964 (July/August 1976).
[50] McRae, E. G., and Hagstrum, H. D., Surface-Structure-Experimental Methods, in reference [14], pp. 57-163.
[51] Seiler, H., Neue Entwicklurgen bei der Abbildung und Analyse von Festkörper-Oberflächen, Chemie-Ing.-Techn. 46, No. 19, 797-804 (1974).
[52] Mayer, J. W., and Turos, A, Comparison of Surface Layer Analysis Techniques, Thin Solid Films 19, No. 1, 1-10 (1973).

[53] Proceedings of the Second International Conference on Solid Surfaces, Kyoto, Japan, March 25-29, 1974, Japanese J. Appl. Phys. Suppl. 2, Part 2, 1974.
[54] Anon., Bibliography on x-ray photoelectron spectroscopy, GCA-McPherson Instrument Product Information (1974).
[55] (a) Hawkins, D. T., Bibliography on Auger-electron spectroscopy applied to surface analysis, in reference [6], pp. 561-575.
(b) Hawkins, D. T., Auger Electron Spectroscopy Bibliography to be published, Plenum Press, N.Y., 1977).
[56] Haas, T. W., Dooley, G. J., Grant, J. T., Jackson, A. G., and Hooker, M. P., Bibliography of Low-Energy Electron Diffraction and Auger-Electron Spectroscopy, in Progress in Surface Science 1, Part 2, 155-236 (1971).
[57] Guide to scientific instruments, Science 190, No. 4216A (Nov. 25, 1975).
[58] 1975-76 Lab Guide, Anal. Chem. 47, No. 10 (Aug. 1975).
[59] Vacuum Technology Directory and Buyer's Guide, Research/Development 27, No. 7, 48-89 (July 1976).
[60] The Analytical Instruments Market (Frost and Sullivan, Inc., New York, May 1974).
[61] Robinson, A. L., Surface Analysis: Multiple Techniques for Monolayers, Science 191, No. 4233, 1253-1256 (March 26, 1976).
[62] Karasek, F. W., Instrument profile - Now and in 1973, Research/Development 23, No. 12, 30-32 (Dec. 1972); Anon., R/D news notes, Research/Development 24, No. 12, 8 (Dec. 1973); Anon., Trends in analytical instruments and equipment, Research/Development 26, No. 2, 20-22 (Feb. 1975).
[63] Marton, L., series editor, Methods of Experimental Physics, Vol. 6 (1959) and Vol. 11 (1974) (Academic Press, New York).
[64] Passaglia, E., editor, Measurement of Physical Properties in Techniques of Metals Research, Vol. 6, Part 1, R. F. Bunshah, series editor (John Wiley and Sons, Inc., N. Y., 1972).
[65] Hofmann, S., Evaluation of Concentration-Depth Profiles by Sputtering in SIMS and AES, Appl. Phys. 9, 59-66 (1976).
[66] Solomon, J. S., and Meyers, V., Auger profile anomalies, American Laboratory 8, No. 3, 31-40 (March 1976).
[67] (a) Winters, H. F., and Coburn, J. W., Influence of the altered layer on depth profiling measurements, Appl. Phys. Lett. 28, No. 4, 176-179 (February 15, 1976);
(b) Pickering, H. W., Ion sputtering of alloys, J. Vac. Sci. Technol. 13, No. 2, 618-621 (Mar./Apr., 1976).
[68] Chang, C. C., Analytical Auger electron spectroscopy, in reference [6], pp. 509-561.
[69] Joshi, A., Davis, L. E., and Palmberg, P. W., Auger electron spectroscopy, in reference [19], pp. 159-222.
[70] Riggs, W. M., and Parker, M. J., Surface analysis by x-ray photoelectron spectroscopy, in reference [19], pp. 103-158.
[71] Hercules, S. H., and Hercules, D. M., Surface characterization by electron spectroscopy for chemical analysis (ESCA), in reference [6], pp. 307-336.
[72] Barrie, A., and Brundle, C. R., A comparison of x-ray induced and electron impact induced photoelectron and Auger spectra: CO adsorption on Mo, J. Electron Spect. 5, 321-338 (Nov./Dec. 1974).
[73] Hercules, D. M., Cox, L. E., Onisick, S., Nichols, G. D., and Carver, J. M., Electron spectroscopy (ESCA): Use for trace analysis, Anal. Chem. 45, No. 11, 1973-1975 (Sept. 1973).
[74] Brinen, J. S., and McClure, J. E., Trace analyses by ESCA-electrochemical measurements, Anal. Lett. 5, No. 10, 737-743 (1972).
[75] Wagner, C. D., Auger parameter in electron spectroscopy for the identification of chemical species, Anal. Chem. 47, No. 7, 1201-1203 (June 1975).
[76] (a) Honig, R. E., and Harrington, W. L., Ion scattering spectrometry below 10 keV, Thin Solid Films 19, No. 1, 43-56 (Dec. 1973);
(b) Buck, T. M., Low-energy ion scattering spectrometry, in reference [19], pp. 75-102.
[77] Buck, T. M., and Poate, J. M., Ion scattering for analysis of surfaces and surface layers, J. Vac. Sci. Technol. 11, No. 1, 289-296 (Jan./Feb., 1974).
[78] (a) Erickson, R. L., and Smith, D. P., Oscillatory cross sections in low-energy ion scattering from surfaces, Phys. Rev. Lett. 34, No. 6, 297-299 (Feb. 10, 1975);
(b) Tolk, N. H., Tully, J. C. Kraus, J., White, C. W., Neff, S. H., Angular dependence of oscillatory structure in low-energy ion-surface scattering, Phys. Rev. Lett. 36, No. 13, 747-750 (March 29, 1976).

[79] Nelson, G. C., Quantitative aspects of ion scattering spectrometry, Anal. Chem. 46, No. 13, 2046-2047 (Nov. 1974).
[80] Mackintosh, W. D., Rutherford Scattering, in reference [6], pp. 403-418.
[81] Werner, H. W., The use of secondary ion mass spectrometry in surface analysis, Surface Science 47, No. 1, 301-323 (Jan. 1975).
[82] Secondary Ion Mass Spectroscopy, Eds. K.F.J. Heinrich and D. E. Newbury, NBS Special Publication 427 (October 1975).
[83] Liebl, H., Ion probe microanalysis, J. Physics E 8, 797-808 (1975).
[84] McHugh, J. A., Secondary ion mass spectrometry, in reference [19], pp. 223-278.
[85] Park, R. L., and Houston, J. E., Soft x-ray appearance potential spectroscopy, J. Vac. Sci. Technol. 11, No. 1, 1-18 (Jan./Feb. 1974).
[86] Anderson, S., and Nyberg, C., Soft x-ray appearance potential spectroscopy of O chemisorbed on Ti, Cr, Fe, and Ni, Solid State Commun. 15, No. 6, 1145-1148 (Sept. 15, 1974).
[87] (a) van Oostrom, A., Surface Analysis by FIM and AP, in reference [8], pp. 353-369; (b) Müller, E. W., The atom probe field ion microscope, in reference [19], pp. 329-378.
[88] Panitz, J. A., Field desorption of helium and neon from tungsten and iridium, J. Vac. Sci. Technol. 12, No. 1, 210-212 (Jan./Feb. 1975).
[89] Greenler, R., The use of thermal desorption, IR spectroscopy, and ellipsometry for surface analyses, in reference [8], pp. 415-428.
[90] Harrick, N. J., and Beckmann, K. H., Internal reflection spectroscopy, in reference [6], pp. 215-245.
[91] Varadi, P. F., Infrared spectroscopy in vacuum and surface studies, Research/Development 24, No. 4, 46-52 (April 1973).
[92] Tompkins, H. G., Infrared reflection-absorption spectroscopy, in reference [19], pp. 447-472.
[93] Lambe, J., and Jaklevic, R. C., Molecular vibration spectra by inelastic electron tunneling, Phys. Rev. 165, No. 3, 821-832 (January 15, 1968).
[94] Skarlatos, Y., Barker, R. C., Haller, G. L., and Yelon, A., Detection of dilute organic acids in water by inelastic tunneling spectroscopy, Surf. Sci. 43, No. 2, 353-368 (June 1974).
[95] Lewis, B. F., Mosesman, M., and Weinberg, W. H., The chemisorption of H_2O, HCOOH, and CH_3COOH on thin amorphous films of Al_2O_3, Surf. Sci. 41, No. 1, 142-164 (January 1974).
[96] Simonsen, M. G., and Coleman, R. V., Inelastic-tunneling spectra of organic compounds, Phys. Rev. B 8, No. 12, 5875-5887 (December 15, 1973).
[97] Duke, C. B., Lipari, N. O., and Laramore, G. E., Surface crystallography via elastic low-energy electron diffraction, J. Vac. Sci. Technol. 11, No. 1, 180-187 (Jan./Feb. 1974).
[98] Duke, C. B., Lipari, N. O., and Laramore, G. E., The atomic geometry of c(2×2) overlayers of sulfur on Ni (100), J. Vac. Sci. Technol. 12, No. 1, 222-225 (Jan./Feb. 1975).
[99] Feder, R., Spin polarization in low-energy electron diffraction from W(001), Phys. Rev. Lett. 36, No. 11, 598-600 (March 15, 1976).
[100] Houston, J. E., and Park, R. L., Low-energy electron diffraction from imperfect surfaces, Surf. Sci. 21, No. 2, 209-223 (July 1970).
[101] Laramore, G. E., Houston, J. E., and Park, R. L., Effect of steps on low-energy electron diffraction profiles, J. Vac. Sci. Technol. 10, No. 1, 196-200 (Jan./Feb. 1973).
[102] Henzler, M., Atomic steps on single crystals: Experimental methods and properties, Appl. Phys. 9, 11-17 (1976).
[103] Somorjai, G. A., The structure and thermodynamics of clean surfaces - principles, in reference [14], pp. 1-55.
[104] Blakely, D.W., and Somorjai, G. A., The dehydrogenation and hydrogenolysis of cyclohexane and cyclohexene on stepped (High Miller Index) platinum surfaces, J. Catalysis 42, No. 2, 181-196 (May 1976).
[105] Gadzuk, J. W., Surface molecules and chemisorption. II. Photoemission angular distributions, Phys. Rev. B 10, No. 12, 5030-5044 (Dec. 15, 1974).
[106] Liebsch, A., Theory of angular resolved photoemission from adsorbates, Phys. Rev. Lett. 32, No. 21, 1203-1206 (May 27, 1974).
[107] Gadzuk, J. W., Angle-resolved photoemission from chemisorbed layers: Further theoretical considerations, Surf. Sci. 53, No. 1, 132-143 (1975).

[108] Waclawski, B. J., Vorburger, T. V., and Stein, R. J., Angular dependence of uv photoelectron distributions for oxygen adsorbed on W(100), J. Vac. Sci. Technol. 12, No. 1, 301-304 (Jan./Feb. 1975).
[109] Egelhoff, W. F., and Perry, D. L., Angular dependence of the photoelectron spectra of hydrogen adsorbed on W(100), Phys. Rev. Lett. 34, No. 2, 93-99 (January 13, 1975).
[110] Traum, M. M., Smith, N. V., and DiSalvo, F. J., Angular dependence of photoemission and atomic orbitals in the layer compound 1T-$TaSe_2$, Phys. Rev. Lett. 32, No. 22, 1241-1244 (June 3, 1974).
[111] Rowe, J. E., Traum, M. M., and Smith, N. V., Measurement of the angle of dangling-bond photoemission from cleaved silicon, Phys. Rev. Lett. 33, No. 22, 1333-1335 (November 25, 1974).
[112] Gadzuk, J. W., Angle resolved Auger surface spectroscopy, Surf. Sci. (to be published, 1976).
[113] (a) Czyzewski, J. J., Madey, T. E., and Yates, J. T., Jr., Angular distributions of electron-stimulated-desorption of ions: Oxygen on W(100), Phys. Rev. Lett. 32, No. 14, 777-780 (Apr. 8, 1974);
(b) Madey, T. E., Czyzewski, J. J., and Yates, J. T., Jr., Ion angular distributions in electron-stimulated desorption: Adsorption of O_2 and H_2 on W(100), Surf. Sci. 49, No. 2, 465-496 (April 1975).
[114] Gersten, J. I., Janow, R., and Tzoar, N., Theory of ion angular distributions in electron-stimulated desorption, Phys. Rev. Lett. 36, No. 11, 610-613 (March 15, 1976).
[115] Brongersma, H. H., and Theeten, J. B., The structure of oxygen adsorbed on Ni(001) as determined by ion scattering spectroscopy, Surf. Sci. 54, No. 2, 519-524 (February 1976).
[116] Froitzheim, H., Ibach, H., and Lehwald, S., Surface sites of H on W(100), Phys. Rev. Lett. 36, No. 26, 1549-1551 (June 28, 1976).
[117] Ibach, H., Horn, K., Dorn, R., and Lüth, H., The adsorption of oxygen on silicon (111) surfaces, Surf. Sci. 38, 433-454 (1973).
[118] Landman, U., and Adams, D. L., Extended x-ray-absorption-fine-structure-Auger process for surface structure analysis: Theoretical considerations of a proposed experiment, Proc. Natl. Acad. Sci. USA 73, No. 8, 2550-2553 (August 1976).
[119] (a) Siegbahn, K., Electron spectroscopy - An outlook, J. Electron Spect. 5, 3-97 (1974);
(b) Pierce, D. T., Applications of UPS and XPS to surface studies, Acta Electronica 18, No. 1, 69-80 (1975).
[120] Powell, C. J., Contrasting valence-band Auger-electron spectra for silver and aluminum, Phys. Rev. Lett. 30, No. 23, 1179-1182 (June 4, 1973).
[121] Ibach, H., and Rowe, J. E., Electron orbital energies of oxygen adsorbed on silicon surfaces and of silicon dioxide, Phys. Rev. B 10, No. 2, 710-718 (July 15, 1974).
[122] Gadzuk, J. W., and Plummer, E. W., Field emission energy distribution (FEED), Rev. Mod. Phys. 45, No. 3, 487-548 (July 1973).
[123] Hagstrum, H. D., The development of ion-neutralization spectroscopy, J. Vac. Sci. Technol. 12, No. 1, 7-16 (Jan./Feb. 1975).
[124] Appelbaum, J. A., and Hamann, D. R., The Electronic Structure of Solid Surfaces, Rev. Mod. Phys. 48, No. 3, 479-496 (July 1976).
[125] Yates, J. T., Jr., Catalysis, Chemical and Engineering News 52, 19-29 (Aug. 26, 1974).
[126] Fischer, T. E., A new look at catalysis, Phys. Today 27, No. 5, 23-28 (May 1974).
[127] Whetten, N. R., Surface physics today, Phys. Today 28, No. 4, 120 (Apr. 1975).
[128] Branscomb, L. M., Promising areas of research in the computer industry, Physics Today 29, No. 1, 54-61 (January 1976).
[129] Morabito, J. M., and Lewis, R. K., The use of Auger Electron Spectroscopy and Secondary Ion Mass Spectrometry in the microelectronic technology, in reference [19], pp. 279-328.
[130] Laudise, R. A., and Nassau, K., Electronic materials of the future: Predicting the unpredictable, Technology Review, p. 61 (Oct./Nov. 1974).
[131] Schnable, G. L., and Keen, R. S., On failure mechanisms in large-scale integrated circuits, Advances in Electronics and Electron Physics 30, 79-138 (Academic Press, N. Y., 1971).
[132] Mattera, L., Component Reliability, Part 1: Failure data bears watching, Electronics 48, No. 20, 91-98 (October 2, 1975); Component Reliability, Part 2: Hearing from vendors and users, Electronics 48, No. 22, 87-94 (October 30, 1975).
[133] Deal, B. E., Identification of integrated circuit process areas amenable to diagnosis and control by analytical beam techniques, in reference [30], pp. 7-20.

[134] Riggs, W. M., and Beimer, R. G., How ESCA pays its way, Chem. Tech. 5, No. 11, 652-659 (November 1975).
[135] McDonald, N. C., Riach, G. E., and Gerlach, R. L., Applications of scanning Auger microanalysis, Research/Development 27, No. 8, 42-50 (August 1976).
[136] Baitinger, W. E., and Amy, J. W., ESCA, Industrial Research 16, No. 6, 60-63 (June 1974).
[137] Karasek, F. W., Surface analysis by Auger spectroscopy, Research/Development 25, No. 10, 48-60 (October 1974).
[138] Anon., Applications of Auger electron spectroscopy, Research/Development 24, No. 7, 36-38 (July 1973).
[139] Weber, R. E., Auger electron spectroscopy for thin film analysis, Research/Development 23, No. 10, 22-28 (October 1972).
[140] Karasek, F. W., Surface analysis by ion sputtering and quadrupole mass spectrometry, Research/Development 24, No. 11, 40-46 (November 1973).
[141] Karasek, F. W., Surface analysis by ISS and ESCA, Research/Development 24, No. 1, 25-30 (January 1973).
[142] Karasek, F. W., SIMS spectra of organic compounds, Research/Development 25, No. 11, 42-46 (November 1974).
[143] Brinen, J. S., Applications of ESCA to industrial chemistry, J. Electron Spect. 5, 377-400 (1974).
[144] Haensel, V., and Burwell, R. L., Jr., Catalysis, Scientific American 225, No. 6, 46-58 (Dec. 1971).
[145] Materials and Man's Needs, Materials Science and Engineering, pp. 204-212 (National Academy of Sciences, Washington, D.C., 1974).
[146] Surface Effects in Controlled Fusion (Proc. of Conference on Surface Effects in Controlled Thermonuclear Fusion Devices and Reactors, Argonne National Laboratory, Argonne, Ill., Jan. 10-12, 1974), Ed. H. Wiedersich, M. S. Kaminsky and K. M. Zwilsky (North-Holland Publishing Co., Amsterdam, 1974).
[147] Vook, F. L., et al., Report to the American Physical Society by the Study Group on Physics Problems Relating to Energy Technologies: Radiation Effects on Materials, Rev. Mod. Phys. 47, Suppl. No. 3, 529-530 (Winter 1975).
[148] Clausing, R. E., Emerson, L. C., Heatherly, L., Colchin, R. J., and Twichell, J. C., Measurement and modification of first-wall surface composition in the Oak Ridge Tokamak (ORMAK), J. Vac. Sci. Technol. 13, No. 1, 437-442 (Jan./Feb. 1976).
[149] Glass, A. J., and Guenther, A. H., The laser damage scene, Electro-Optical Systems Design, pp. 28-32 (June 1976).
[150] Glass, A. J., and Guenther, A. H., Laser Induced Damage in Optical Materials: 6th ASTM Symposium (Summary report of 6th ASTM-ONR-NBS Symposium on Laser Induced Damage in Optical Materials, National Bureau of Standards, Boulder, Colo., May 22-23, 1974), Appl. Optics 14, No. 3, 698-715 (Mar. 1975).
[151] Mills, G. A., Conversion of coal to gasoline, Industrial and Engineering Chemistry 61, No. 7, 6-17 (July 1969).
[152] Osborn, E. F., Coal and the present energy situation, Science 183, No. 4124, 477-481 (Feb. 8, 1974).
[153] Weiss, A. H., Luss, D., Mears, D. E., and Heck, R., Industrial needs in catalysis, Chem. Eng. Prog. 69, No. 5, 59-64 (1973); Fischer, T. E., Contributions of surface physics to catalysis, CRC Critical Reviews in Solid State Sci. 6, No. 4, 401-411 (1976).
[154] Hearing before the Joint Committee on Atomic Energy, Congress of the United States, Ninety-third Congress, 1st session, Consideration and Discussion of Atomic Energy Commission Report containing recommendations for five-year, $10 billion energy research and development program, Dec. 11, 1973, pp. 94-95, 110-111, 340-345, 381-390. (U.S. Government Printing Office, Washington, D.C., 1974).
[155] Squires, A. M., Clean fuels from coal gasification, Science 184, No. 4134, 340-346 (Apr. 19, 1974); Squires, A. M., Chemicals from coal, Science 191, No. 4228, 689-700 (Feb. 20, 1976).
[156] (a) Maugh, T. H., Hydrogen: Synthetic fuel of the future, Science 178, No. 4063, 849-852 (Nov. 24, 1972);
(b) Winsche, W. E., Hoffman, K. C., and Salzano, F. J., Hydrogen: Its future role in the Nation's energy economy, Science 180, No. 4093, 1325-1332 (June 29, 1973).
[157] Robinson, A. L., Energy storage (II): Developing advanced technologies, Science 184, No. 4139, 884-887 (May 24, 1974).

[158] (a) Chynoweth, A. G., Electronic Materials: Functional Substitutions, Science 191, No. 4227, 725-732 (Feb. 20, 1976);
(b) Hillig, W. B., New materials and composites, Science 191, No. 4227, 733-739 (Feb. 20, 1976);
(c) Claasen, R. S., Materials for advanced energy technologies, Science 191, No. 4227, 739-745 (Feb. 20, 1976).
[159] Townsend, P. D., Kelly, J. C., and Hartley, N.E.W., Ion Implantation, Sputtering and Their Applications (Academic Press, N. Y., 1976).
[160] Physics in Perspective, Vol. II, Part B, The Interfaces, pp. 1069-1075 (National Academy of Sciences, Washington, D.C., 1972).
[161] Griffith, O. H. et al., Photoelectron microscopy: A new approach to mapping organic and biological surfaces, Proc. Natl. Acad. Sci. USA 69, No. 3, 561-565 (March 1972).
[162] Slodzian, G., Some problems encountered in secondary ion emission applied to elementary analysis, Surf. Sci. 48, No. 1, 161-186 (1975).
[163] Blakely, D. W., Kozak, E. I., Sexton, B. A., and Somorjai, G. A., New instrumentation and techniques to monitor surface reactions on single crystals over a wide pressure range (10^{-8}-10^{5} Torr) in the same apparatus, J. Vac. Sci. Technol. 13, No. 5, 1091-1096 (Sept./Oct. 1976).
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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

An analysis is given of the National Measurement System for Surface Properties. Emphasis is placed on the properties needed to characterize a solid surface, particularly surface composition, surface atomic structure and surface electronic structure; these characteristics directly affect many important surface properties or processes that occur on surfaces (e.g., electrical and optical properties, adhesion, bonding, catalytic activity, plating, durability, corrosion, decoration, segregation, lubrication and reactivity). The above three forms of surface characterization are widely utilized in surface-science experiments while measurements of surface composition are routinely made to solve a wide variety of problems in the semiconductor, chemical, petroleum and metallurgical industries for applications ranging from process and device development, process control, process evaluation to failure analysis. Surface-characterization measurements in government laboratories support a variety of agency missions. Surface science and surface technology have both grown rapidly in the past ten years, and further growth is expected. At this time, there is a complete lack of standards, standard procedures, and standard materials to support surface-characterization measurements. In short, there is no established national system for the measurement of surface properties. Recommendations for NBS action are given to improve and extend the measurement services required to promote surface science and surface technology and thereby to establish a satisfactory system for the measurement of surface properties.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* National Measurement System for Surface Properties; surface atomic structure; surface characterization; surface composition; surface electronic structure; surface properties

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